Hole transporting materials for methylammonium lead halide (CH₃NH₃PbX₃) perovskite solar cells

Krishna, Anurag

2017

Krishna, A. (2017). Hole transporting materials for methylammonium lead halide (CH₃NH₃PbX₃) perovskite solar cells. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69457>

<https://doi.org/10.32657/10356/69457>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**HOLE TRANSPORTING MATERIALS FOR
METHYLAMMONIUM LEAD HALIDE
($\text{CH}_3\text{NH}_3\text{PbX}_3$) PEROVSKITE SOLAR CELLS**

ANURAG KRISHNA

**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

2016

**HOLE TRANSPORTING MATERIALS FOR
METHYLAMMONIUM LEAD HALIDE
(CH₃NH₃PbX₃) PEROVSKITE SOLAR CELLS**

ANURAG KRISHNA

Interdisciplinary Graduate School
Energy Research Institute @ NTU (ERI@N)

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

08-08-2016

.....

.....

Anurag Krishna

Abstract

Organic-inorganic lead halide perovskites have shown promise as cost effective high-performance material for solar cells. Hole transport materials (HTMs) are currently the bottleneck for the realization of efficient cost effective and stable devices. In this work, novel hole-transporting molecules based on triptycene (T101, T102 and T103), furan (F101) and silafluorene (S101) cores were synthesized using short routes with high yields are presented. In HTMs T101, T102 and T103 triptycene core is linked with diarylamine, triarylamine and thiophene-linked triarylamine sidechains, respectively. The bulky and twisted structure of triptycene provides high thermal stability, high glass transition temperature (T_g) and high solubility in common organic solvents. HTM F101 consists of an electron-rich furan core linked to triphenylamine moieties. The planar structure and smaller size of the O atom in the ring was expected to result in closer intermolecular π - π stacking, which could be beneficial for enhancing the hole transport and also increase the lifetime of charge carriers. In HTM S101 an electron rich silafluorene core is linked to triphenylamine moieties and hexyl chains attached to the silicon atom to produce high solubility inorganic solvents and so improve processing.

Quantum calculations were performed to predict the opto-electronic properties and were found to be consistent with the experimental data. The power conversion efficiency (PCE) of the perovskite solar cells (PSCs) fabricated with T101, T102, and T103 as HTM was 8.42%, 12.24% and 12.38% respectively, as compared to 12.87% for spiro-OMeTAD. These results show that the performance of these three materials in perovskite solar cells was profoundly influenced by the sidechains. The devices based on F101 produced high PCE of 13.12%, which was higher than the efficiency obtained using spiro-OMeTAD (13%). The F101 HTM based device exhibited a J_{SC} of 19.63 mA/cm² and a remarkably high V_{OC} of 1.1 V. The charge carrier dynamics of perovskite/ HTM

interface which gives insight into the charge transfer process, were studied via steady state and time resolved PL. From PL steady state spectra, it was evident that both HTMs significantly quench the perovskite emission signal, with HTM F101 demonstrating slightly better PL quenching efficiency, ~ 97%, compared to spiro-OMeTAD (~ 93%). Both HTMs spiro-OMeTAD and F101 showed similar decay lifetimes of ~ 1 ns. These results suggest that furan is potentially an excellent unit for incorporation in HTMs and furans should be further investigated as replacements for thiophene units in HTMs. The devices fabricated with HTM S101 shows a PCE of ~ 11% which is comparable to that ($\eta = 12.3\%$) obtained with spiro-OMeTAD. From the PL spectra it was evident that both HTMs significantly quench perovskite emission signal, with HTM spiro-OMeTAD having a slightly better PL quenching efficiency (ca. 93%) relative to S101 (ca. 89%). Time-resolved PL measurements of $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-OMeTAD samples showed a decay time of 0.8 ns whereas $\text{CH}_3\text{NH}_3\text{PbI}_3$ /S101 samples showed a longer decay life time of 1.1 ns. This indicates that both HTMs are quenching the holes but spiro-OMeTAD has a slightly better hole extraction ability as compared to S101. These results suggest silafluorene derivatives can produce at least comparable cost-per-unit power performance to spiro-OMeTAD.

HTMs based on different design principles were synthesized and their properties and device performances studied in detail. The triptycene based HTMs are bulky, star shaped and non-planar with high T_g . By contrast the furan and silafluorene-based HTMs, i.e., F101 and S101 are linear and planar, respectively and possess lower T_g . This suggests high T_g is not necessary for high efficiency, though more detailed device stability tests need to be performed to see if it is important for extending lifetime. The performance of all these molecules having different dimensional symmetry (star shaped, linear and planar molecules) in PSCs is quite encouraging for the development of cost effective technologies.

Acknowledgements

First of all, I would like to extend my gratitude to my supervisors Assoc. Prof. Andrew Grimsdale and Assoc. Prof. Cesare Soci and my mentor Prof. Subodh Mhaisalkar for support, guidance, patience and motivation in all stages of my Ph.D. Their profound knowledge and yearning for ground breaking research has always been a motivating factor for me throughout my work at NTU.

I would like to thank all the lab-mates and colleagues who helped by sharing valuable experiences on all the aspects linked with lab affairs, including Dr Li Hairong, Andrey Lunchev, Dr. Dharani Sabba, Dr. Hemant Mulmudi, Dr. Annalisa Bruno, Dr. Francesco Maddelena, Dr. Pablo P. Boix. Moreover, thanks to my friends Dr. Ranjan, Sudhanshu, Dr. Anish, Apoorva, Nebojsha, Kristina, Natasa, Li and Himanshu who stood with me and provided me support in tough times.

Many thanks also to all the technical staffs in MSE and ERIAN to provide warmest help when I was doing the experiment works.

A special thanks to my family -parents, brother and sister. Your blessings, sacrifices and support have helped me to reach my goals.

Finally, I would like to thank NTU for the granting of a postgraduate Research Scholarship.

Table of Contents

Abstract	i
Acknowledgements	iii
Table of Contents	v
Table Captions	ix
Figure Captions	xi
Abbreviations	xix
 Chapter 1 Introduction	 1
1.1 Hypothesis/problem statement.....	2
1.2 Objectives and Scope.....	4
1.3 Dissertation Overview	5
1.4 Findings and Outcomes/Originality.....	8
References.....	9
 Chapter 2 Literature Review	 11
2.1 Overview	12
2.2 Mesoscopic Solar Cells.	12
2.2.1 Liquid and Solid State Dye Sensitized Solar Cells.....	13
2.2.2 Organic-Inorganic Halide Perovskite Solar Cells.....	15
2.3 Hole-Transporting Materials in Perovskite Solar Cells.....	18
2.3.1 Inorganic HTMs.....	18
2.3.2 Organic Polymeric HTMs.....	18
2.3.3 Organic Small molecule HTMs.....	21

2.4	Questions to answer based on literature.....	36
2.5	PhD in context of literature.....	38
	References.....	39
 Chapter 3 Experimental Methodology		49
3.1	Rationale for selection of Materials.....	50
3.2	Synthesis techniques: reaction type, purification, analysis.....	51
3.2.1	Suzuki coupling	51
3.2.2	Column chromatography for purification of small organic molecules...	53
3.3	Characterization: Principles and Analysis	55
3.3.1	NMR Spectroscopy.....	55
3.3.2	Mass spectrometry (MALDI-TOF-MS)	58
3.3.3	Differential scanning calorimetry (DSC).....	59
3.3.4	Electrochemical method: Cyclic Voltammetry.....	60
3.3.5	Ultraviolet-Visible (UV-Vis) Spectroscopy.....	62
3.3.6	Time resolved photoluminescence (TRPL)	65
3.3.7	Photovoltaic Measurements.....	67
3.4	Computational Methods.....	68
3.5	Device Fabrication.....	69
	References.....	70
 Chapter 4 Novel Hole Transporting Materials Based on Triptycene Core for High Efficiency Mesoscopic Perovskite Solar Cells.....		73
4.1	Introduction	76
4.2	Experimental Methods.....	76
4.2.1	Synthesis	76
4.2.2	Quantum Chemistry Calculations	81
4.2.3	Materials and Equipment.....	81
4.2.4	Device Fabrication.....	81
4.3	Results and Discussion.....	81

4.3.1	Structural Characterization.....	81
4.3.2	Modeling and Quantum Chemistry Calculations.....	90
4.3.3	Thermal, optical and electrochemical properties	93
4.3.4	Device performance.....	96
4.4	Conclusion and Outcomes.....	100
	References.....	101

Chapter 5 Facile Synthesis of a Furan–Arylamine Hole-Transporting Material for High-Efficiency Mesoscopic Perovskite Solar Cells.....103

5.1	Introduction.....	104
5.2	Experimental.....	105
5.2.1	Synthesis.....	105
5.2.2	Computational Methods	105
5.2.3	Materials and Equipment.....	106
5.2.4	Device Fabrication.....	106
5.3	Results and Discussions.....	107
5.3.2	Structural Characterization.....	107
5.3.3	Quantum Chemistry Calculations.....	109
5.3.3	Optoelectronic and electrochemical properties.....	113
5.3.4	Device performance.....	115
5.3.5	Steady State and Time-resolved PL.....	118
5.4	Conclusion and Outcomes.....	120
	References.....	120

Chapter 6 Facile Synthesis of Hole Transporting Material with Silafluorene Core for Efficient Mesoscopic CH₃NH₃PbI₃ Perovskite Solar Cells.....123

6.1	Introduction	124
6.2	Experimental.....	125
6.2.1	Synthesis.....	125

6.2.2	Materials and Equipment	126
6.2.3	Computational Methods.....	126
6.2.4	Device Fabrication.....	126
6.3.1	Results and Discussions.....	127
6.3.1	Structural Characterization.....	127
6.3.2	Quantum Calculations.....	129
6.3.3	Thermal, optical and electrochemical properties.....	132
6.3.4	Device performance.....	136
6.3.5	Steady State and Time-resolved PL Quenching	138
6.4	Conclusion and Outcomes.....	139
	References.....	140
Chapter 7	Discussion and Future Work.....	143
7.1	Discussion and Summary.....	144
7.2.1	Preliminary work and suggestions for future work	149
7.2.2	Stilbene Based linear HTM (SB101).....	149
7.2.3	Triptycene Based HTM (T104).....	154
7.2.4	Adamantane Based HTM.....	155
7.2.5	Furan Based HTMs.....	156
7.2.6	Organo-silicon based HTMs.....	157
	References.....	158
	Appendix	159

Table Captions

Table 2.1	Summary of the polymer type HTMs.....	21
Table 2.2	Summary of organic spiro type small molecule HTMs.....	25
Table 2.3	Summary of organic star shaped small molecule HTMs.....	29
Table 2.4	Summary of linear type small molecule HTMs.....	33
Table 2.5	Summary of other type of small molecules.....	35
Table 4.1	Summary of the calculated optical and electronic properties.....	93
Table 4.2	Summary of the experimental optical and electronic properties.....	94
Table 4.3	Summary of device various parameters; current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), efficiency (η).....	98
Table 5.1	Intermolecular electronic coupling, distance and transfer rate and hole mobility of F101 crystal.....	111
Table 5.2	Intermolecular electronic coupling, distance and transfer rate and hole mobility of Spiro-OMeTAD crystal.....	112
Table 5.3	Optical, and electrochemical properties of F101 and spiro-OMeTAD.....	115

Table 5.4	Summary of device parameters; open circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and efficiency (η).....	116
Table 5.5	Time resolved photoluminescence characterization of the $CH_3NH_3PbI_3$ perovskite. The data were collected at the maximum of the $CH_3NH_3PbI_3$ perovskite emission (760 nm).....	119
Table 6.1	Intermolecular electronic coupling, distance and transfer rate and hole mobility of S101 crystal (Fig 6.6a).....	131
Table 6.2	Intermolecular electronic coupling, distance and transfer rate and hole mobility of Spiro-OMeTAD crystal (Fig 6.6b).....	132
Table 6.3	Thermal, optical and electrochemical properties of S101 and spiro-OMeTAD.....	134
Table 6.4	Summary of device parameters; open circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and efficiency (η).Area=0.2 cm^2	137
Table 6.5	Time resolved photoluminescence characterization of the $CH_3NH_3PbI_3$ perovskite.....	137
Table 7.1	Optical and electrochemical properties of SB101.....	154
Table A1	Summary of the cost analysis of spiro and triptycene core.....	161
Table A2	Summary of the cost analysis of spiro and silafluorene core...	164

Figure Captions

Figure 2.1	Schematic views of the components and operating principles of a liquid electrolyte dye-sensitized solar cell.....	14
Figure 2.2	(a) Device architecture of ss-DSSC; (b) Operating principle of ss-DSSC.....	14
Figure 2.3	(a) Crystal structure of cubic perovskite with general chemical formula ABX_3 . (b) Device architecture of mesoscopic perovskite solar cells. (c) Schematic representation of charge-transfer processes in perovskite solar cells.....	17
Figure 2.4	Chemical structures of polymers used as HTM in PSCs.....	20
Figure 2.5	Energy level diagram showing HOMO levels of various polymeric HTMs.....	21
Figure 2.6	Additives (dopants and salts) used in HTMs.....	22
Figure 2.7	Spiro-type small molecule HTMs for PSCs.....	23
Figure 2.8	Energy level diagram showing HOMO levels of spiro-type HTMs.....	25
Figure 2.9	Star shaped small molecule HTMs for PSCs.....	26
Figure 2.10	Energy level diagram showing HOMO levels of star shaped HTMs.....	28

Figure 2.11	Linear Shaped small molecule HTMs for PSCs.....	30
Figure 2.12	Energy level diagram showing HOMO levels of linear shaped HTMs.....	32
Figure 2.13	Other type of HTMs for PSCs.....	33
Figure 2.14	Energy level diagram showing HOMO levels of other type of HTMs.....	36
Figure 3.1	General chemical formula for Suzuki coupling.....	52
Figure 3.2	Catalytic cycle for Suzuki coupling.....	53
Figure 3.3	Schematic illustration of working process of column chromatography.....	54
Figure 3.4	Ranges of chemical shifts (δ , ppm) for ^1H in compounds with different substituents.....	56
Figure 3.5	^1H NMR spectra of chloroethane.....	58
Figure 3.6	Illustration working mechanism of MALDI-TOF.....	59
Figure 3.7	Typical reversible electrochemical loops in a CV scan.....	60
Figure 3.8	Illustrates the general pattern of energy levels and the fact that the transitions are brought about by the absorption of different amounts of energy.....	63

Figure 3.9	Schematic diagram of a spectrophotometer.....	64
Figure 3.10	Schematic diagram showing working of TR-PL set up.....	66
Figure 3.11	Schematic diagram showing working of solar simulator.....	67
Figure 4.1	Chemical structure of Spiro-OMeTAD.....	75
Figure 4.2	Chemical structures of T101, T102 and T103.....	76
Figure 4.3	¹ H NMR spectrum of compound 3.....	82
Figure 4.4	¹³ C NMR spectrum of compound 3.....	82
Figure 4.5	¹ H NMR spectrum of Compound 4.....	83
Figure 4.6	¹³ C NMR spectrum of compound 4.....	83
Figure 4.7	¹ H NMR spectrum of T101.....	84
Figure 4.8	¹³ C NMR spectrum of T101.....	85
Figure 4.9	¹ H NMR spectrum of T102.....	86
Figure 4.10	¹³ C NMR spectrum of T102.....	87
Figure 4.11	¹ H NMR spectrum of compound 8.....	88
Figure 4.12	¹³ C NMR spectrum of compound 8.....	88

Figure 4.13	^1H NMR spectrum of T103.....	89
Figure 4.14	^{13}C NMR spectrum of T103.....	90
Figure 4.15	Calculated and experimental ionization potential (IP), HOMO, LUMO levels and electronic density distributions of Spiro-OMeTAD and triptycene-based HTMs T101, T102 and T103.....	91
Figure 4.16	Calculated and experimental absorption spectra of triptycene-based materials (T101, T102 and T103).....	92
Figure 4.17	(a) Cyclic Voltammograms of Spiro-OMeTAD, T101 , T102 and T103 with ferrocene as the reference; (b) Differential Scanning Calorimetry (DSC) curves of T101 , T102 and T103	95
Figure 4.18	(a) Cross-sectional SEM of the device; (b) band diagram for the device with HTMs T101 , T102 , T103 and Spiro-OMeTAD.....	95
Figure 4.19	(a) Current density vs. voltage curve; (b) IPCE spectra of the perovskite solar cell devices with T101 , T102 , T103 and Spiro-OMeTAD as HTM, respectively.....	96
Figure 4.20	(a) Recombination resistance and (b) Transport resistance of HTMs in the full solar cell determined by electrochemical impedance spectroscopy.....	98
Figure 5.1	Chemical structures of F101.....	105

Figure 5.2	^1H NMR spectrum of F101.....	107
Figure 5.3	^{13}C NMR spectrum of F101.....	108
Figure 5.4	MALDI-TOF mass spectra of F101.....	108
Figure 5.5	(a) Chemical Structure of F101, electronic density distribution of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for F101; (b) Chemical Structure of Spiro-OMeTAD, electronic density distribution of LUMO and HOMO for Spiro-OMeTAD.	109
Figure 5.6	Different hole transfer pathways for possible crystal structures (a) C2/C, (b) P21/C and (c) P212121 of F101 molecule.....	111
Figure 5.7	Different hole transfer pathways for possible crystal structure (a) P21/C, (b) P21 and (c) P212121 of Spiro-OMeTAD molecule.....	112
Figure 5.8	(a) Absorption Spectra for Spiro-OMeTAD and F101; (b): Cyclic voltammogram for Spiro-OMeTAD and F101; (c) Band diagram for the device with new HTM F101 and Spiro-OMeTAD and (d) Cross-sectionnal SEM image of device fabricated with F101.....	113
Figure 5.9	Transfer characteristics in the p-channel type FET of (a) spiro-OMeTAD and (b) F101. These characteristics were measured at $V_g = -40\text{V}$	115

Figure 5.10	Current density vs. voltage curve under AM 1.5G illumination (100 mW/cm ²); (b) Recombination resistance extracted from fitting of the EIS results under illumination for perovskite solar cells with F101 and Spiro-OMeTAD as the HTM.....	116
Figure 5.11	IPCE spectra of the device with HTMs F101 and Spiro-OMeTAD.....	117
Figure 5.12	(a) The steady-state photoluminescence (PL) spectra and (b) Time-resolved PL spectra of CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ PbI ₃ /Spiro-OMeTAD and CH ₃ NH ₃ PbI ₃ /F101.	118
Figure 6.1	Chemical structures of S101.....	125
Figure 6.2	¹ H NMR spectrum of S101.....	127
Figure 6.3	¹³ C NMR spectrum of S101.....	128
Figure 6.4	MALDI-TOF mass spectra of S101.....	128
Figure 6.5	(a) Chemical structure of S101, electronic density distribution of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for S101; (b) chemical structure of spiro-OMeTAD, electronic density distribution of LUMO and HOMO for spiro-OMeTAD.....	129
Figure 6.6	(a) Hole transfer pathways for possible crystal structure (1) C2/C, (2) P1 and (3) P212121 of S101 molecule; (b) hole transfer pathways for possible crystal structure (1) C2/C, (2) P21 and (3) P212121 of Spiro-OMeTAD molecule.....	131

Figure 6.7	(a) Absorption spectra for spiro-OMeTAD and S101, (b) cyclic voltammograms for spiro-OMeTAD and S101, c) band diagram for the device with new HTM S101 and spiro-OMeTAD, and d) cross-sectional SEM image of device fabricated with S101.....	134
Figure 6.8	Differential Scanning Calorimetry (DSC) curves for S101.....	135
Figure 6.9	Transfer characteristics in the p-channel type FET of (a) spiro-OMeTAD and (b) S101. These characteristics are measured at $V_g = -40V$	135
Figure 6.10	Current density vs. voltage curve under AM 1.5G illuminations (100 mWcm^{-2}).....	137
Figure 6.11	The steady-state photoluminescence (PL) spectra and (b) time-resolved PL spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{S101}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{spiro-OMeTAD}$	139
Figure 7.1	Chemical structure of SB101.....	150
Figure 7.2	Synthetic route of SB101.....	150
Figure 7.3	^1H NMR spectra of SB101.....	151
Figure 7.4	MALDI-TOF mass spectra of SB101.....	152
Figure 7.5	Quantum Modeling for SB101 showing distribution of HOMO and LUMO state.....	152

Figure 7.6	(a) Absorption Spectra for Spiro-OMeTAD and S101; (b): Cyclic voltammogram for Spiro-OMeTAD and SB101.....	153
Figure 7.7	Chemical structure of T104.....	154
Figure 7.8	Chemical structures of HTMs A101 and A102.....	155
Figure 7.9	Chemical structure of HTM F102.....	156
Figure 7.10	Chemical structures of HTM S102-S105.....	157

Abbreviations

HTM	Hole Transporting Material
HTL	Hole Transporting Layer
PSC	Perovskite Solar Cell
PCE	Power Conversion Efficiency
DSSC	Dye Sensitized Solar Cell
ss-DSSC	Solid State Dye Sensitized Solar Cell
PSC	Perovskite Solar Cell
OFET	Organic Field Effect Transistor
NMR	Nuclear Magnetic Resonance
V _{oc}	Open Circuit Voltage
J _{sc}	Short Circuit Current
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
IPCE	Incident photon to current efficiency
FF	Fill Factor
I-V	Current-voltage
J-V	Current density-voltage
FTO	Flourine doped tin oxide
TiO ₂	Titanium dioxide
ACN	Acetonitrile
EIS	Electrochemical impedance spectroscopy
SEM	Scanning electron microscopy
FESEM	Field emission scanning electron microscopy
UV-Vis	Ultraviolet visible
AM	Air mass
R _{ct}	Recombination resistance

PL	Photoluminescence
TR-PL	Time resolved Photoluminescence
CE	Counter Electrode
TCO	Transparent Conducting Oxide
CV	Cyclic Voltammetry

Chapter 1

Introduction

This section starts by explaining the rationale behind the current work. The aim of the research is to develop novel hole transporting materials (HTMs) for lead halide sensitized mesoscopic solid state solar cells that not only show impressive photo conversion efficiency (PCE) but are also cost effective as compared to the current standard HTM spiro-OMeTAD. Currently there is no specific design principle/set of rules for designing HTMs for mesoscopic solid state cells. Therefore, it is intended, by using the results of experimental and theoretical studies on the new materials in comparison with existing materials, to develop a set of possible principles and rules for designing HTMs. The section then summarizes what is found in each chapter of the thesis, describes the objectives and scope, and what is original about the work.

1.1 Hypothesis/Problem Statement

Organic–inorganic metal halide perovskites, in particular methyammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have emerged as very promising light harvesting materials for high performance and low cost perovskite solar cell photovoltaic technology [1-3]. The performance of perovskite solar cells (PSCs) strongly affected not only by the quality of the perovskite film but also by the use of charge transporting layers. In particular if a hole transporting material (HTM) is not used high efficiencies cannot be obtained. However current HTMs suffer deficiencies which continue to hold back realization of the potential of PSCs. The highest device efficiencies are currently being obtained when using spiro-OMeTAD (or its derivatives) as HTM. However, this material suffers from two major problems. The first is its high cost, due to its multistep and inefficient synthesis and to the need for costly purification. The other is its poor charge carrier mobility which requires the use of hygroscopic dopants to obtain high efficiencies. These reduce significantly the lifetime of devices as they promote degradation of the perovskite by atmospheric water. While many other HTMs are known and have been tested in PSCs, to date they have generally shown significantly lower performance. Hence if PSC technology is to realize its potential, it is imperative to find alternative HTMs to spiro-OMeTAD, which have better or comparable efficiency and are more economical to produce. A major scientific problem is that the development of such HTMs is currently a matter of (sometimes blind) trial and error as there is no set of design rules that might be used to help in designing a good HTM. More understanding of HTMs is needed to establish the sorts of structure property relationships needed to be able to rationally design good HTMs. The factors that need consideration in this regard are the following:

- Various kinds of structures have been proposed for HTMs which show good performance in perovskite solar cells. However, there is no clear set of rules

for the design of a good HTM. It is proposed that by systematic comparison of the properties of HTMs and the devices using them it should be possible to derive insights into how to rationally design HTMs to achieve optimum photovoltaic properties.

- Glass transition temperature (T_g) is suspected to be an important parameter for HTMs as solar cells can become hot during operation and so a high T_g may be desirable to avoid phase changes in the HTM which may cause device instability. So by comparing similar materials with different T_g it should be possible to establish the relationship, if any, between the T_g of an HTM and the device performance and stability.
- The open circuit voltage (V_{OC}) of the perovskite solar cells is determined mainly by the HOMO level of the HTM. Hence by making HTMs with different HOMO levels one can study the influence of HOMO level and resulting V_{OC} on the device performance.
- The fill factor of the device depends on the series resistance, which itself depends on the mobility of the HTM. Hence the design and synthesis of HTMs with high mobility to minimize the series resistance and achieve high fill factor is desirable.
- In general the HTMs consist of an aromatic or heteroaromatic core to which is attached one or more di- or tri- arylamine functional groups. Various types of cores can lead to different thermal, optical and electronic properties. Hence the correlation between the different types of cores, and the HTM and device properties should be established. The functional group used in HTMs can be linked directly to the core or electron rich groups such as a thiophene can be inserted between the core and the functional group. By making a series of related HTMs with same core but with different linkers it should be possible to elucidate the effects of such linkers on the materials and device properties and so obtain useful structure-property relationships for rational design of HTMs.

- Solubility of HTMs is critical as perovskite solar cells are solution processed. Hence in the HTM the core and the attached functional group should be such that HTMs have high solubility in organic solvents.
- The study of charge carrier dynamics and lifetime is critical to understand the working the HTMs. So far not much emphasis has been given to this aspect. It is hypothesized that the study of the carrier lifetime using techniques like photoluminescence (PL) quenching and correlate this with device performance will aid molecular design.
- Density function theory (DFT) and quantum calculations can be used to predict the opto-electronic properties such as energy levels, hole mobility, etc., of the HTMs. It is hypothesized that correlation of the calculated and experimental results will also aid in molecular design.
- Since the perovskite solar cell is solution processed, therefore the HTM deposition condition such as spin speed and time, solution concentration, post deposition annealing temperature, etc., need to be optimized for optimum performance of HTM layer and the photovoltaic device. This aspect lies outside the scope of this work and so where possible all the new HTMs will be used in devices constructed using the same conditions as for spiro-OMeTAD devices which will be used as standard for comparison.

1.2 Objectives and Scope

The aim of this work is to design and synthesize novel HTMs and test their performance in perovskite solar cells and study their structure-property relationship to evolve a set of design principles for the rational design of good HTMs. This thesis covers various HTMs with different structure and design principles. Comprehensive computational, structural, thermal, optical, electrochemical and electrical characterizations have been performed to obtain data from which the design principle of efficient HTMs may be developed. In particular perovskite solar cell (PSC) devices have been fabricated employing the

novel HTMs to evaluate their performance in comparison with spiro-OMeTAD. Further, charge carrier dynamics at the perovskite/HTM interface have been studied employing PL and time-resolved PL, to obtain insight into the interfacial charge transfer process.

1.3 Dissertation Overview

This thesis addresses design and development of hole transporting materials for perovskite solar cells. The thesis has been organized into 7 chapters.

Chapter 1 discusses the problem statement and rationale driving the research work. The challenges and issues related to HTMs are discussed in a broader context. The specific goals and scope of the thesis are conceptualized.

Chapter 2 provides a comprehensive literature survey of the field. The historical perspective of the problem is presented along with the relevant current research developments. Important issues and gaps related to the design of HTMs and their performance in PSC devices have been identified and serve as a basis for this thesis work.

Chapter 3 discusses the research methodology employed during the course of the current research work. The principles of the various instruments used for synthesis, characterization and device fabrication/testing and the associated analysis details are discussed. A brief introduction to the underlying physics of the research techniques used and methods involved is also provided.

Chapter 4 describes the synthesis of series of hole transporting materials (T101, T102 and T103) based on a triptycene core with diarylamine, triarylamine and thiophene- linked triarylamine side chains, respectively. The bulky and twisted structure of triptycene has some similarity to that of spiro-OMeTAD and provides

high thermal stability, high glass transition temperature (T_g) and high solubility in common organic solvents. The results of quantum calculations carried out to predict the optoelectronic properties of the HTMs have been discussed. The structure of HTM was confirmed by NMR and MALDI-TOF mass spectroscopy. Detailed thermal, optoelectronic and electrochemical characterization of the three HTMs have been performed. In this work the performance of these three materials (T101, T102 and T103) in perovskite solar cells as the HTMs was investigated in comparison to similar devices using spiro-OMeTAD as HTM in order to determine the effects of the different sidechains on the device performance. The electrochemical impedance spectroscopy was performed to further study the device data.

Chapter 5 describes the synthesis of a furan based HTM (F101) consisting of an electron-rich furan core linked to triphenylamine moieties. The smaller size of the Oxygen (O) atom in the ring compared to the Sulphur (S) atom in previously reported thiophene-based HTMs should result in closer intermolecular π - π stacking, which could be beneficial for enhancing the hole transport and also increase the lifetime of charge carriers. Furthermore, the small molecular size of the HTM could lead to better pore filling of the mesoporous TiO_2 layer loaded perovskite. Quantum calculations were carried out to predict the optoelectronic properties of the HTM. The structure of HTM was confirmed by NMR and MALDI-TOF mass spectroscopy. Comprehensive electrical (mobility), optoelectronic and electrochemical characterization were done prior to device fabrication. Mesoscopic perovskite solar cells were fabricated using F101 HTM and spiro-OMeTAD was investigated. The charge carrier dynamics of perovskite/HTM interface which give insight in to the interfacial charge transfer process were studied employing steady state and time resolved PL. PL analysis illustrated that F101 has hole extraction capability similar and comparable to the standard HTM spiro-OMeTAD.

Chapter 6 discusses synthesis of a novel HTM (S101) based on an electron rich silafluorene core to which are linked triphenylamine moieties, with hexyl chains attached to the silicon atom to produce high solubility in organic solvents and improve the solution processing. The silafluorene unit is anticipated to enhance the stability of the HTM and devices using it. The S101 molecule has a planar structure which is desirable for promoting intramolecular π -delocalization and intermolecular π - π stacking, which favor both charge carrier mobility and lifetime, and boost device efficiency. The optoelectronic properties of the HTM S101 were theoretically estimated from the quantum calculations. After the synthesis the structure of HTM was confirmed by NMR and MALDI-TOF mass spectroscopy. The thermal, optoelectronic and electrochemical characteristics were probed by differential scanning calorimetry, UV-Vis spectroscopy and cyclic voltammetry, respectively. The hole mobility was determined from the field effect transistor (FET) made using the HTM. Mesoscopic perovskite solar cells were fabricated using this HTM and the PCE was investigated. The charge carrier dynamics of perovskite/HTM interface which gives insight in to the charge transfer process were investigated by employing the steady state and time resolved PL. The interpretation of the PL data reveals that the standard HTM spiro-OMeTAD has slightly better hole extraction capability than the HTM S101.

Chapter 7 draws together the threads of the thesis with summary of the previous three chapters, based on the connections between experimental results and hypotheses put forward in the project design. Based on the results obtained during the current work, issues relevant to the future work have been identified and prospective work direction is presented.

1.4 Findings and Outcomes/Originality

In course of the current study, HTMs based on various different design principles were synthesized and used in perovskite solar cells. The original scientific contributions achieved during this Ph. D. work are enumerated below.

- The first HTMs (T101, T102 and T103) based on a triptycene core have been synthesized and tested as HTMs in mesoscopic perovskite solar cells. The results obtained from these HTMs show that the choice of functional side group and/or linker has major effects on device performance thus helping to establish design principles for high performance HTMs.
- The first furan based HTM (F101) has been made and tested successfully tested in PSCs. PSCs incorporating this HTM show impressive PCE and has charge carrier extraction capability comparable to the standard HTM spiro-OMeTAD. The results suggest that furans should be further investigated as replacements for thiophene units in HTMs.
- The first silafluorene-based HTM (S101) has been designed and synthesized. S101 has a deep highest occupied molecular orbital (HOMO) energy level offering the possibility of higher V_{OC} . The PCE of the device with S101 as the HTM is slightly smaller than the one with spiro-OMeTAD as HTM. However, the deep HOMO energy level offers possibility of enhancement in the V_{OC} after the refinement and tuning of the device parameters.
- HTMs based on various different design principles were synthesized and their properties and device performances studied in detail. The triptycene based HTMs are bulky and have high T_g whereas furan based HTM F101 and silafluorene-based S101 are planar with comparatively low T_g . However, comparison of the performance and stability of the devices using these HTMs suggests that T_g may not be a critical factor for the design of new HTMs.

References

- [1] H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel, and N.-G. Park, *Sci. Rep.* **2012**, 2, 591(1-7).
- [2] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Science* **2012**, 338, 643-647.
- [3] M. A. Green, A. Ho-Baillie, and H. J. Snaith, *Nat. Photonics* **2014**, 8, 506-514.

Chapter 2

Literature Review

This literature review begins with a brief overview of the evolution of mesoscopic solar cells, from liquid state DSSC to perovskite solar cells. The focus is mainly on the HTMs responsible for hole extraction and transport in PSCs, which are one of the essential components of efficient devices. The range of HTMs being used in PSCs are then discussed in detail. After summarizing reported HTMs, the gaps between their current performance and what is needed for the intended application are discussed, to place the current work in context.

2.1 Overview

At present most of the world's energy needs are generated from the fossil fuels such as oil, natural gas and coal. These non-renewable energy sources face a number of challenges such as rising prices, constantly growing energy demand, growing environmental concerns and decreasing fossil fuel reserves. Consequently, for the last several decades efforts have been made to look for alternative energy sources that are cheaper, environment friendly and renewable. In this regard, clean and sustainable solar energy has emerged as one of the most rapidly growing renewable sources of energy. One of the most effective methods of converting solar energy in to electricity is a solar cell which is based on the photovoltaic effect. Various solar cells such as silicon solar cells, organic photovoltaic cells, dye-sensitized solar cells (DSSC), etc. are used to covert solar energy in to electrical energy. However despite showing increasingly high efficiency the use of these cells on a large scale has been limited. This is mainly because of their high manufacturing cost and limited lifetimes. So, there is a need for developing alternative solar cell technologies, which are economical and robust. Recently, organic-inorganic perovskites have emerged as high efficiency cost effective photovoltaic materials. Within three years of the first report, a PCE of 22.1% was reported for perovskite solar cells (PSCs). Herein, a brief overview of the evolution of mesoscopic solar cells which include DSSC, solid state DSSC and PSCs is provided. Then a detailed and comprehensive discussion on various kinds of hole transporting materials which are an important component of PSCs is given.

2.2 Mesoscopic Solar Cells.

This section discusses the basic aspects of Liquid and Solid State Dye Sensitized Solar Cells and Organic-Inorganic Halide Perovskite Solar Cells.

2.2.1 Liquid and Solid State Dye Sensitized Solar Cells

In 1991, Grätzel and O'Regan reported a mesoscopic dye sensitized solar cell (DSSC), using a ruthenium complex as dye adsorbed onto a nanocrystalline titania (TiO_2) mesoporous film, with an impressive PCE of $\sim 7\%$ [1]. This discovery opened a new frontier in the race for developing solar energy harvesting technologies. A typical liquid-based DSSC consists of a photoanode, which is usually glass coated with a transparent conductive oxide (TCO) such as fluorine-doped tin oxide (FTO), a mesoporous TiO_2 layer with the sensitizer (dye) adsorbed onto it, an electrolyte containing a redox couple, and a platinized counter electrode as shown in Fig. 2.1 [2,3]. The operation principle of a DSSC is illustrated in Figure 2.1. The dye absorbs photons and as a result electrons are excited from the HOMO to the LUMO of the dye. Then the electrons are injected from the LUMO into the conduction band of the TiO_2 , which is an electron transporter. These electrons are transported through the mesoporous film of TiO_2 by diffusion processes and are collected at the corresponding anode. The oxidized dye molecules are regenerated by the liquid electrolyte (typically an iodide/iodine redox couple) which infiltrates through the pores of the mesoporous film and is in interfacial contact with the dye molecules. At the counter electrode, the oxidized species of the electrolyte is reduced by the electrons which have flowed through the external circuit, and hence the whole cycle is completed. So far impressive PCEs of up to 13% for devices made in a laboratory and 10% in prototype modules have been achieved [4,5]. However, the problems of leakage, instability and the corrosive nature of the redox electrolyte have emerged as the major impediments towards the commercialization of DSSCs [6]. To get rid of these problems, attention has been shifted to solid state devices in which the liquid electrolyte is replaced by a solid hole transporting material (HTM). Consequently, in 1998, Bach et al. reported the first solid state dye sensitized solar cells (ssDSSC) with a PCE of 0.74% using an organic HTM 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-

OMeTAD) [7]. The device architecture and operation principle of ssDSSC are shown in Fig. 2.2. This was the first major breakthrough in the development of ss-DSSCs. By optimizing and tuning the various device components by changing dyes, modifying the TiO_2 and developing new dopants for spiro-OMeTAD, in 2011 a record efficiency of 7.2% was achieved by the Grätzel group [8]. To date spiro-OMeTAD remains the best performing HTM in solid state devices. In 2012, the substitution of dyes with organic–inorganic lead halide perovskite absorbers in ss-DSSCs has revolutionized the thin-film photovoltaic technologies [9,10].

Figure 2.1 Schematic views of the components and operating principles of a liquid electrolyte dye-sensitized solar cell.

Figure 2.2 (a) Device architecture of ss-DSSC; (b) Operating principle of ss-DSSC.

2.2.2 Organic-Inorganic Halide Perovskite Solar Cells

Perovskites refer to a class of materials that have the general ABX_3 chemical formula, where A and B are two cations of very different sizes and X an anion. The crystal structure of perovskite is shown in Fig. 2.3a [11,12]. The most commonly used perovskite for photovoltaic application is methylammonium lead halide, where the halogens are I, Cl or Br. In 2009, Miyasaka and co-workers reported the first use of organolead halide perovskite as sensitizer in liquid-based DSSCs [13]. They used $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ as light absorbers, in combination with a standard iodine-based liquid electrolyte in DSSCs. PCEs of merely 3.1% and 3.8% were obtained for the tribromide and triiodide perovskites, respectively. In 2011, Park et al. further improved the performance of the liquid-based $CH_3NH_3PbI_3$ solar cell to 6.5% by modifying the surface of TiO_2 and the method used for deposition of the perovskite [14]. Unfortunately, the perovskites dissolve in liquid electrolytes and device degrades rapidly. In 2012, major breakthrough was made when Grätzel et al. and Snaith et al. reported first solid-state perovskite solar cells (PSCs) using $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$ as light absorbers deposited onto a mesoporous TiO_2 layer and spiro-OMeTAD as HTM, leading to PCEs of 9.7% and 7.6%, respectively [9,10]. Since then the growth in efficiencies has been unprecedentedly rapid so that a certified PCE of 22.1% has recently been achieved in short period [15]. Enormous research efforts have been dedicated to the development of PSCs, which include development of new device architectures [16–27], application of different n-type nanostructures [28–35], chemically tuning the perovskite composition [36–46], and developing new deposition techniques for high-quality perovskite films [47–54].

The device architectures of perovskite solar cells (PSCs) are analogous to ss-DSSCs, as shown in Fig. 2.3b. The fabrication procedure for PSCs is as follows. First, a compact TiO_2 blocking layer is coated on a FTO substrate. Then a mesoporous layer of TiO_2 is subsequently deposited on top of the compact TiO_2

blocking layer. After that perovskite film is spin-coated on the mesoporous TiO_2 layer, followed by the deposition (from vapour or solution) of a thin HTM layer. Lastly, a metal electrode, such as gold (Au) or silver (Ag) is deposited by thermal evaporation on top of the HTM. The charge-transfer processes involved in PSCs are shown in Fig. 2.3c [55]. Under illumination (1), the perovskite is excited and electrons are injected into conduction band of TiO_2 (2), the holes generated in perovskite are transferred to the HTM (3). These charges are then collected at the anode and cathode of the solar cell. But, undesirable charge-transfer processes such as recombination of the charges and back charge-transfer processes at TiO_2 /perovskite/HTM interface (shown in red color in Fig. 2.3c) also occur. The HTM layer plays a critical role in preventing the undesirable charge transfer processes. Apart from extracting holes from the perovskite and transporting them to the cathode, the HTM also helps to prevent the recombination losses at the TiO_2 /perovskite/HTM interface which leads to improvement in the performance of the device. Consequently, research on HTMs has been one of the hot topics in PSCs.

Figure 2.3 (a) Crystal structure of cubic perovskite with general chemical formula ABX_3 . (b) Device architecture of mesoscopic PSCs. (c) Schematic representation of charge-transfer processes in PSCs.

2.3 Hole-Transporting Materials in Perovskite Solar Cells

An HTM for PSCs should primarily meet the following requirements: (1) a compatible HOMO energy level relative to valence band energy (VBE) of perovskite for efficient hole transfer; (2) sufficient hole mobility; (3) good solubility and film forming properties, (4) good thermal and photochemical stability and (5) low cost. Several HTMs have been developed and investigated in PSCs, which are composed of inorganic and organic hole-conductors. Organic HTMs can be divided into two categories: small molecule and polymeric hole-conductors [56]. Following on from ss-DSSC experience spiro-OMeTAD has long been the benchmark HTM against which other materials have been compared.

2.3.1 Inorganic HTMs

The development in inorganic HTMs has been rather slow compared to other class of HTMs. The main reason for slow progress is the limited choice of inorganic materials. Materials such as CuI (PCE=6%) [57], NiO (PCE =11.6%) [58], and CuSCN (PCE=12.4%) [59] have been used as HTM in PSCs. These HTMs are cheap and stable under ambient conditions, but they show inferior performance as compared to the organic HTMs.

2.3.2 Organic Polymeric HTMs

In past conjugated polymers have been used for LEDs, OPVs and FETs application [60-62]. Polymeric HTMs are known with high hole mobility values and good transport properties. Heo et al. [63] reported the use of a number of conjugated polymers as HTMs in PSCs (Fig. 2.4). These included materials such as poly(3-hexylthiophene (P3HT), poly[N-9-heptadecanyl-2,7-carbazole-alt-3,6-bis(thiophen-5-yl)-2,5-dioctyl-2,5-dihydropyrrolo-3,4pyrrole-1,4-dione]

(PCBTDPP), poly-[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT), poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophene-diyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), which are known as good electron donors in solar cells and/or as high mobility materials in p-type transistors and poly(triarylamine) (PTAA) which contains the triarylamine moiety seen in many small molecule HTMs [56]. Among these polymers, PTAA demonstrated the highest PCE ~12%. Later the same group used a mixed-halide perovskite with PTAA and reported a certified PCE of 16.2%. Recently, a certified PCE of 17.9% has been reported with PTAA as HTM [64]. Chen et al. [65] reported a P3HT/MWNT (multi-walled carbon nanotube) composite as a HTM which showed PCE of 6.45%. This was better than PCE obtained with the pristine P3HT (PCE=4.1%). The increase in PCE was due increase in fill factor which was attributed to the enhanced conductivity of the composite due inclusion of MWNTs. P3HT-functionalized single-walled carbon nanotubes (SWNTs) was reported as HTM by Habisreutinger and co-workers [66]. PCE of up to 15.3% was obtained. Xiao et al. [67] reported that polyaniline (PANI) as HTM, produced a PCE of 7.34%. PANI here acted as both sensitizer and HTM. The PCE reduced only slightly (from 7.3% to 6.7%) After 1000 hours, PCE reduced slightly from 7.3% to 6.7% which device has good stability under ambient conditions. Ryu et al. [68] reported a triarylamine-based polymer HTM (PIF8-TAA) for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite. The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite has a deeper HOMO level than the $\text{CH}_3\text{NH}_3\text{PbI}_3$ which leads to a larger band gap and so less light absorption at longer wavelengths. However, a moderate PCE (6.7%) and a high voltage output (1.4 V) were obtained. Kwon et al. [69] reported polymer HTMs with a hydrophobic DPP based polymer (PDPPDBTE) with a deep HOMO energy level of -5.4 eV and good hole mobility of $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Ryu et al. [68] reported a triarylamine-based polymer HTM (PIF8-TAA) for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite. The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite has a deeper HOMO level than the $\text{CH}_3\text{NH}_3\text{PbI}_3$ which leads to a larger band gap and so less light

absorption at longer wavelengths. However, a moderate PCE (6.7%) and a high voltage output (1.4 V) were obtained. Kwon et al. [69] reported polymer HTMs with a hydrophobic DPP based polymer (PDPPDBTE) with a deep HOMO level of -5.4 eV and good hole mobility of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This polymer showed a PCE of 9.2% when iodoperovskite solar cells were fabricated; under similar conditions spiro-OMeTAD and P3HT showed PCE of 7.6% and 6.3%, respectively. Yang and co-workers [70] reported HTMs TFB and PFB which are polyfluorene-based polymers that contain fluorene and arylamine groups. TFB-based devices demonstrated promising PCEs (10.9–12.8%), which were comparable to the corresponding values for Spiro-OMeTAD (9.8–13.6%). Ameen et al. [71] reported polyaniline nanoparticles (PANINPs) as an efficient HTM with $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs and obtained 6.29% efficiency. Except PTAA none of the polymeric HTMs were able to outperform spiro-OMeTAD, moreover most of these are high in cost, since their synthesis is complex and low yielding and suffers from batch-to-batch inconsistency. Therefore, more focus has been given to small molecule organic HTMs, which are often simpler in design, and can be easier to synthesize and cheaper than the best performing polymeric HTMs. Polymers are also harder to purify as compared with small molecules. The chemical structure of polymers used in PSCs is depicted in Fig. 2.4 and energy level diagrams showing HOMO energy levels are shown in Fig. 2.5.

Figure 2.4 Chemical structures of polymers used as HTM in PSCs.

Figure 2.5 Energy level diagram showing HOMO levels of various polymeric HTMs.

Table 2.1 Summary of the polymer type HTMs.

HTM	E_{HOMO} (eV)	Dopants	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	Ref.
P3HT	-5.2	LiTFSI, TBP	12.6	0.73	73	6.7	63
PTAA	-5.14	LiTFSI, TBP	19.6	1.11	74	16.2	63
PCPDTBT	-5.3	LiTFSI, TBP	10.3	0.77	67	5.3	63
PCDTBT	-5.45	LiTFSI, TBP	10.5	0.92	44	4.2	63
PANI	-5.27	LiTFSI, TBP	18	0.88	40	6.3	71
PFB	-5.1	LiTFSI, TBP	13	0.91	64	8	70

2.3.3 Organic small molecule HTMs

As compared to the inorganic and polymeric HTMs, much more work has been done on small molecule HTMs. This is because small molecule HTMs allow more freedom in their design and are often simple to synthesize. In the design of small molecule hole conductors, triarylamine moieties seem to be an integral part of the HTM. The nitrogen atom in triarylamine moieties acts as a doping site, which can be stabilized through conjugation with neighbouring phenyl rings. The intermolecular distance increases due to non-planar conformation of the triarylamine which leads to low hole mobility of the molecule. However, it makes the molecules amorphous and makes them more suitable as HTMs in PSCs,

though the amorphous nature of these molecules also reduces their charge carrier mobility. To improve the charge carrier mobility of the small molecule HTMs various additives such as lithium salts, cobalt salts, 4-tert-butylpyridine (TBP) etc. are often used (Fig. 2.6). The most widely used and generally best performing HTM has been spiro-OMeTAD and so this review of small molecule HTMs starts with spiro-molecules.

Figure 2.6 Additives (dopants and salts) used in HTMs [56a].

2.3.3.1 Spiro-type HTMs

The chemical structure of spiro-type small molecules used as HTMs is shown in Fig. 2.7. Spiro compounds have been used as emissive or charge transporting materials in organic light emitting diodes (OLEDs) [56b]. The spiro centre makes the material bulky, amorphous and provides thermal stability, which are good properties because it helps formation of very smooth and defect free films. Kim et al. [9] first reported a perovskite sensitized mesoscopic solar cell using spiro-OMeTAD as HTM. The solar cell device exhibited a large photocurrent (J_{SC}) of 17.0 mA/cm^2 , V_{OC} of 0.89 V, FF of 0.62, and a PCE of 9.7%. Later workers by optimizing the device were able to raise the efficiency of PSCs using spiro-

OMeTAD to 20% [72]. While spiro-OMeTAD remains the benchmark HTM for PSCs as for ss-DSSCs, it has a significant cost problem. The relatively long and low yielding synthesis of spiro-OMeTAD and the need to purify it by sublimation make it very expensive (~SGD1000/g) which significantly increases the costs of PSCs using it. With the aim of improving the performance of the PSC, Seok and co-workers [73] synthesized derivatives of spiro-OMeTAD with the -OMe groups on different positions on the aromatic rings. The optoelectronics properties of spiro-OMeTAD were found to be altered by changing the position of the -OMe groups. The PSC fabricated using the ortho-substituted derivative of spiro-OMeTAD (po-Spiro-OMeTAD) showed a PCE of 16.7% which was better as compared to the para-(spiro-OMeTAD) and meta- (pm-spiro-OMeTAD) substituted derivatives. The reason for high PCE was an increase in the FF in the device using po-spiro-OMeTAD. This was attributed to the higher LUMO level of po-spiro-OMeTAD which blocks electron flow in to the metal electrode, leading to an increase in fill factor.

Figure 2.7 Spiro-type small molecule HTMs for PSCs.

Saliba et al. [74] reported a molecularly engineered HTM with a simple dissymmetric fluorene–dithiophene (FDT) core substituted by N,N-di-p-methoxyphenylamine donor groups, which can be easily modified, providing the blueprint for a family of potentially low-cost hole-transport materials. The devices fabricated with HTM FDT showed PCE of 20.2% which compare favorably with control devices with spiro-OMeTAD. Thus, this new hole conductor has the potential to replace spiro-OMeTAD. The authors suggest that there can be an additional interaction between the dithiophene FDT core and the perovskite surface, possibly mediated by the thiophene-iodine interaction, which may impart a stronger adhesion and enhanced interfacial coupling between FDT and perovskite. This may lead to more effective hole transfer.

Franckevičius et al. [75] reported a HTM (spiro-CPDT) based spiro-fluorene-bithiophene as core and triarylamine derivatives as functional groups. When used as HTM in PSCs, a PCE of 13.4% was achieved without the use of any dopants and additives, which was comparable to PCE (15.0%) of spiro-OMeTAD based devices using p-type dopants. Furthermore, the device based on the spiro-CPDT HTM showed a slightly higher V_{OC} of 0.971 V compared to a spiro-OMeTAD ($V_{OC} = 0.951$ V) based device. Spiro-CPDT is thus an excellent starting point for design of dopant-free HTMs PSCs, if the factors allowing such high undoped performance can be elucidated. Ganesan et al. [76] reported a new spiro HTM (PST1) with spiro-bipropylenedioxythiophene as spiro core. The PSC fabricated with HTM PST1 exhibited J_{SC} of 17.63 mAcm^{-2} , V_{OC} of 1.02 V, FF of 0.73 and an overall PCE of 13.4%. Under similar fabrication conditions, the device with spiro-OMeTAD as HTM showed a slightly lower PCE of 12.2%. The slightly higher PCE in PST1 based devices was due to higher V_{OC} in PST1 based device compared to that of spiro-OMeTAD-based devices, which can be attributed to the deeper HOMO energy level in PST1. The energy level diagram showing the HOMO levels of spiro-type HTMs is depicted in Fig. 2.8 and the summary of their performance in PSCs is provided in table 2.2.

Figure 2.8 Energy level diagram showing HOMO levels of spiro-type HTMs.

Table 2.2 Summary of organic spiro type small molecule HTMs.

HTM	E_{HOMO} (eV)	Dopants	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PC E (%)	Ref.
spiro-OMeTAD	-5.22	LiTFSI, TBP, FK209	20.0	0.99	73	15.0	73
po-spiro-OMeTAD	-5.31	LiTFSI, TBP	21.2	1.02	78	16.7	73
pm-spiro-OMeTAD	-5.22	LiTFSI, TBP	21.1	1.01	65	13.9	73
PST-1	-5.15	LiTFSI, TBP, FK102	17.6	0.91	73	12.2	76
Spiro-CPDT	-5.0	FK102	19.3	0.97	72	13.4	75
FDT	-5.16	LiTFSI, TBP, FK209	22.7	1.14	76	20.2	74

2.3.3.2 Star Shaped HTMs

Star shaped molecules have been used as emissive and hole transporting materials in OLEDs [56,77]. The idea behind these molecules is that like the spiro-centres into the materials just discussed, the non-planar star shaped molecular structure prevents easy packing of molecules and so hinders crystallization [77]. These materials are thus amorphous and hence ideal for solution processed organic electronic devices. However, these molecules typically have low mobility, so need to be doped with additives such as lithium salts, TBP or cobalt salts to improve the mobility.

Figure 2.9 Star shaped small molecule HTMs for PSCs.

Grimsdale and co-workers [78] synthesized two TPA-based HTMs with tetrasubstituted thiophene (H111) and tetrasubstituted bithiophene (H112) core units. The synthesis of both these HTMs is shorter and more efficient and economical than that of spiro-OMeTAD. Both of these HTMs exhibited PCEs over 15% and outperformed spiro-OMeTAD devices made as controls. Choi et

al. [79] have synthesized a HTM (OMeTPA-FA) based fused quinolizino acridine which showed a promising PCE of up to 13.6%. Do et al. [80] synthesized two star-shaped HTMs (triazine-Ph-OMeTAD and triazine-Th-OMeTAD) based on a triazine unit. This molecular system is donor- π -acceptor type which includes an electron rich diphenylamino unit and an electron-deficient triazine unit. A thiophene (triazine-Th-OMeTAD) or phenyl (triazine-Ph-OMeTAD) unit is used as a π -linker between the triazine and diphenylamino unit. The HTM with thiophene as π -linker showed better PCE (12.51%) compared to the HTM with phenyl π -linker (10.90%). Spiro-OMeTAD based devices produced a PCE of 13.45% under similar conditions. Recently Cabau et al. [81] synthesized a novel small molecule, tetra{4-[N,N-(4,40-dimethoxydiphenylamino)] phenyl}ethene (TAE-1), with an excellent yield of 72%. This HTM was used without addition of any additives/dopants and a very promising PCE of ~ 11% has been reported.

Recently, Gratia et al. [82] reported methoxydiphenylamine-substituted carbazole based HTM (V886), with performance similar to that of spiro-OMeTAD. The high solubility in organic solvents and simple two-step synthesis made V886 very attractive for the commercial prospects of PSCs. The perovskite devices fabricated with V886 showed a maximum PCE of 16.9%, with an average PCE exceeding 14%. The measured J_{SC} is 21.4 mA/cm², V_{OC} is 1.09 V, and FF is 0.73. Under similar conditions a maximum PCE of 18.4% was obtained with spiro-OMeTAD as HTM. Park et al. [83] reported PCP-TPA, a [2,2]paracyclophane triarylamine-based HTM. The synthesis of PCP-TPA is shorter and more high yielding than that of spiro-OMeTAD, and it showed a high hole mobility due to effective intermolecular aggregation in the film state. When used as a HTM in perovskite solar cells, a PCE of 17.6% was obtained. High performance coupled with straightforward synthesis makes PCP-TPA an excellent candidate for cost effective PSCs. Rakstys et al. [84] reported four star-shaped HTMs (K122, K131, K145 and K133) based on planar triazatruxene cores

and electron-rich methoxy-engineered side arms. These HTMs were obtained from relatively cheap starting materials by adopting facile preparation procedure, without using expensive and complicated purification techniques. The PSCs based on K131 showed a remarkable PCE of 18.3%, which was slightly higher than PCE obtained with spiro-OMeTAD (17.9%). Very recently, Malinauskas et al. [85] reported three HTMs based on methoxydiphenylamine-substituted fluorene (V852, V859 and V862). The PSCs fabricated with V859 and V862, showed very high PCE of 19.47% and 19.96%, under similar conditions spiro-OMeTAD showed a PCE of 18.25%. Furthermore, these HTMs don't require a complex and expensive synthesis procedure and could be synthesized from readily available commercial starting materials using a simple two step method. High performance and simple synthetic procedure make these HTMs very attractive for commercial prospects of PSCs. The chemical structure of various star shaped HTM molecules are shown in Fig. 2.9 and the corresponding energy levels showing the HOMO levels are depicted in Fig. 2.10. The characteristics of the PSCs incorporating these molecules as HTMs are summarized in table 2.3.

Figure 2.10 Energy level diagram showing HOMO levels of star shaped HTMs.

Table 2.3 Summary of organic star shaped small molecule HTMs.

HTM	E _{HO} MO (eV)	Dopants	V _{OC} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref.
KR131	-5.30	LiTFSI, TBP, FK209	1.145	20.7	77	18.3	84
KR145	-5.06	LiTFSI, TBP, FK209	0.96	18.4	67	11.9	84
KR133	-5.26	LiTFSI, TBP, FK209	1.133	20.4	72	16.8	84
V886	-5.27	LiTFSI, TBP, FK209	1.09	21.4	73	16.9	82
V859	-5.23	LiTFSI, TBP, FK209	1.120	23.3	75	19.47	85
V862	-5.22	LiTFSI, TBP, FK209	1.139	22.5	77	19.96	85
PCP-TPA	-5.33	LiTFSI, TBP	1.04	22.0	78	17.8	83
triazine-Th- OMeTAD	-5.04	-	0.92	20.7	66	12.5	80
OMeTPA- FA	-5.14	LiTFSI, TBP, FK209	0.97	21.0	67	13.6	79
H111	-5.31	LiTFSI, TBP, FK102	1.08	19.8	72	15.4	78
H112	-5.29	LiTFSI, TBP, FK102	1.07	20	71	15.2	78

2.3.3.3 Linear small molecule HTMs

Figure 2.11 Linear Shaped small molecule HTMs for PSCs.

Several linear small molecules have been used as HTMs in PSCs. Fig. 2.11 shows series of small linear molecules. These structures have benzene or heterocycles as cores connected to one or two terminal triphenylamine derivatives. Compared to spiro and star shaped HTMs, linear shaped HTMs are simpler in structure and usually are simpler to synthesize. The linear molecules are also more planar which leads to more effective π - π stacking, hence improving the hole transport properties.

A major advance in the design of small molecule HTMs for PSCs came when Li et al. [86] reported a very simple new HTM (H101), having an ethylenedioxythiophene (EDOT) core linked with triarylamine moieties (H101). Devices using this material displayed a PCE of up to 13.8% which was

comparable to that obtained with spiro-OMeTAD in control devices. The DSC measurements showed glass transition temperature (T_g) of H101 was 73°C, which is lower than that of the spiro-OMeTAD (125°C), but the stability of the devices kept at 70°C were similar suggesting that low T_g materials could also work equally well. The synthesis of H101 is much easier and more efficient as compared to that of spiro-OMeTAD and the estimated cost of its production is significantly lower. Later Docampo and co-workers [87] modified H101 and reported new HTM EDOT-OMeTPA, in which EDOT core was linked with azomethine. The objective of this work was to reduce the synthesis cost of HTM. Authors report that EDOT-OMeTPA is much cheaper to make than H101 and both HTMs have comparable performance. Xu et al. [88] synthesized two HTMs (X19 and X51) based on carbazole cores. The carbazole is substituted with diphenylamine at 3-, and 6- positions and with a phenyl group on the carbazole nitrogen. The hole mobilities and conductivities of X19, X51 and spiro-OMeTAD were 1.19×10^{-4} , 1.51×10^{-4} , $5.31 \times 10^{-5} \text{ cm}^2/\text{Vs}$ and 2.88×10^{-5} , 1.05×10^{-4} , $8.67 \times 10^{-5} \text{ S/cm}$, respectively. X51 showed superior conductivity and mobility to X19. Also X51 showed almost three times higher hole mobility than spiro-OMeTAD. The PSCs fabricated using X51 exhibited a higher PCE of 9.8% compared to X19 (7.6%); under similar conditions spiro-OMeTAD showed a PCE of 10.2%. Li and co-workers [89] reported TPA based HTMs with a butadiene π -conjugated system. The hole mobilities of the HTMs which are $2.98 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and $1.27 \times 10^{-3} \text{ cm}^2/\text{Vs}$, which is two orders of magnitude higher than mobility of spiro-OMeTAD. The performance of the HTMs was moderate. HTM1 showed a higher PCE (11.63%) compared to HTM2 (11.34%). Under similar conditions a spiro-OMeTAD based devices showed a PCE of 12.08%.

Choi et al. [90] reported two new HTMs TAZ-[MeOTPA]₂ and TAZ-[MeOTPAth]₂ based on 4-phenyl-1,2,4-triazole core, incorporating two electron-rich diphenylamino side arms, through direct linkage or thiophene bridges, respectively. These HTMs have a donor-acceptor type molecular

structure which exhibits effective intramolecular charge transfer, improving the hole-transporting properties. The structural modification of HTMs by thiophene bridging might increase intermolecular π - π stacking and conjugation length. The PSCs fabricated using TAZ-[MeOTPA]₂ and TAZ-[MeOTPAth]₂ showed PCE of 10.9% and 14.4%, respectively, which was comparable to that obtained using spiro-OMeTAD. Abate et al. [91] reported two HTMs PEH-1 and PEH-2 based on silolothiophene linked to triarylamine. In PEH-1 the Si atom is substituted with two hexyl chains whereas in PEH-2 the substituents are phenyl groups which makes PEH-2 more bulky. The DSC measurements showed that PEH-2 had a T_g higher than 100°C, whereas PEH-1 was crystalline at room temperature, which means that PEH-2 will be thermally more stable. PEH-2 and PEH-1 based devices showed PCE up to 13.5% and 11.7%, respectively. Both the HTMs showed inferior performance compared to spiro-OMeTAD (15.2%). Though the PCE of HTMs is lower than spiro-OMeTAD, devices based on PEH-2 showed good stability, whereas, the devices based on PEH-1 degraded rapidly. These authors claim that high stability of PEH-2 based devices was due to the high T_g and superior thermal stability of the HTM used. It has been reported that silole units can enhance the photostability of conjugated polymers containing them, and so enhance the lifetimes of solar cells using the resulting polymers [92]. The energy level diagram of the linear shaped molecules showing the HOMO energy levels is depicted in Fig. 2.12 and a summary of the PSCs incorporating them is summarized in table 2.4.

Figure 2.12 Energy level diagram showing HOMO levels of linear shaped HTMs.

Table 2.4 Summary of linear type small molecule HTMs.

HTM	E_{HOMO} (eV)	Dopants	V_{OC} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref.
H101	5.16	LiTFSI, TBP, FK102	1.05	19.1	65	13.2	86
PEH-1	-5.16	LiTFSI, TBP, FK209	0.96	19.4	72	11.7	91
PEH-2	-5.17	LiTFSI, TBP, FK209	0.97	19.4	72	13.5	91
X19	-5.43	LiTFSI, TBP	0.76	17.1	58	7.6	88
X51	-5.49	LiTFSI, TBP	0.88	16.8	66	9.8	88
TAZ- [MeOTPAH] ₂	-5.08	LiTFSI, TBP	1.0	21.8	66	14.4	90

2.3.3.4 Other type of organic small molecule HTMs

Figure 2.13 Other type of HTMs for PSCs.

Most small molecule HTMs are spiro, star shaped or linear type, but several other small molecules have been studied. The structures of these molecules do not fall under any of the categories discussed above. Fig. 2.13 shows chemical structure of some of such HTMs.

Jeon et al. [93] synthesized three HTMs (Py-A, Py-B and Py-C) based on a pyrene core. The pyrene core was linked with various numbers of N,N-di-p-methoxyphenylamine moieties. The devices fabricated with Py-A showed poor PCE of 3.3%, because the HOMO level of Py-A was very deep and close to perovskite valance band which lead to poor hole injection as there was not enough driving force. The best devices fabricated using Py-B and Py-C as a HTM showed a PCE of 12.3 and 12.4%, respectively which was comparable to PCE obtained with spiro-OMeTAD (12.7%). This like the development of H101 above suggested that very simple structures can prove useful as HTMs in PSCs. Liu et al. [94] reported the HTM (TTF-1) based on tetrathiafulvalene. This HTM has extremely simple structure and does not contain a TPA moiety. The PSC fabricated using TTF-1 showed PCE over 11% without the use of any dopants or additive. The devices with TTF-1 had good stability; the lifetime of these PSCs under ambient conditions being three times higher than spiro-OMeTAD based PSCs used as control devices.

Kazim et al. [95] reported a new HTM based on a pentacene derivative (TIPS-pentacene). The pentacene is substituted with bis(triisopropylsilyl)ethynyl (TIPS) groups at the C-6 and C-13 positions. TIPS side groups stabilized the HOMO energy level, and improved solubility in organic solvents, allowing it to be used as a HTM for PSCs. The device fabricated with TIPS-pentacene without any dopants or additives showed a PCE of 11.5% but surprisingly, the device using TIPS-pentacene doped with LiTFSI and tBP as additives a showed lower PCE of 8.2 %. Ramos et al. [96] synthesized two HTMs (HMDI and HPDI) based on a triazatruxene core. The HOMO energy level of these HTMs was tuned by

introducing electron-rich alkoxy side groups. These HTMs were simple in synthesis, soluble, thermally stable and had suitable HOMO for hole transfer. The HPDI based devices gave a PCE of ~ 11%. Lim et al. [97] reported a HTM (C12-carbazole) based indolocarbazole. The C12- carbazole showed high hole mobility of $5.1 \times 10^{-2} \text{ cm}^2/\text{V.s}$ which is three orders magnitude higher than the mobility of spiro-OMeTAD ($5.31 \times 10^{-5} \text{ cm}^2/\text{V.s}$). The device fabricated with C12-carbazole showed PCE of ~ 11.26% which higher than the PCE shown by spiro-OMeTAD (9.62) based devices. Wang et al. [98] reported a carbazole (R01) HTM. R01 is synthesized via a facile route consisting of only two steps from inexpensive commercially available materials. Furthermore, R01 exhibits higher hole mobility and conductivity than the spiro-OMeTAD. PSCs fabricated with R01 produce a PCE of 12.03% which is comparable to that obtained in devices using Spiro-OMeTAD. The energy level diagram showing HOMO levels of other type of HTMs is depicted in Fig. 2.14 and the characteristics of PSCs incorporating them is summarized in table 2.5.

Table 2.5 Summary of other type of small molecules.

HTM	E _{HOMO} (eV)	Dopants	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PC E (%)	Ref.
Py-A	-5.41	LiTFSI, TBP, FK209	0.89	10.8	34	3.3	93
Py-B	-5.25	LiTFSI, TBP , FK209	0.95	20.4	64	12.3	93
Py-C	-5.11	LiTFSI, TBP, FK209	0.89	20.2	69	12.4	93
TTF-1	-5.05	-	0.86	19.9	64	11.0	94
R01	-5.30	MY11, FK209	0.98	17.9	69	12.0	98
HPDI	-5.41	LiTFSI	0.98	19.2	58	10.8	96
C12- carbazole	-5.29	LiTFSI, TBP	0.86	21.1	62	11.3	97
TIPS- Pentacene	-5.40	LiTFSI, TBP	0.91	20.8	60	11.5	95

Figure 2.14 Energy level diagram showing HOMO levels of other type of HTMs.

2.4 Questions to answer based on literature

As discussed in the previous section, an array of HTMs have been developed for PSCs, which includes various novel organic small molecule hole transporters, conducting polymers and inorganic semiconductors. The highest efficiencies are currently being obtained when using spiro-OMeTAD (or its derivatives) as HTM. However, the high cost of spiro-OMeTAD due its tedious synthesis and purification and its low hole mobility, several alternative HTMs have been developed with the goal to replace spiro-OMeTAD. Although considerable progress has been made in the development of alternative HTMs, some critical issues including device stability still need to be addressed in the future in order to further improve the performances of PSC devices by developing new HTMs. It should be noted that maximizing efficiency is not necessarily the main criterion to be considered as from the ultimate commercial perspective the dominant criterion will be cost per unit power produced. Thus a slightly less efficient device using a much cheaper HTM is likely to be preferred by industry, especially if it has a long lifetime.

In this literature review, the progress of development of HTMs in PSCs has been summarized and key issues must be addressed to further improve the performance of PSCs has been identified and discussed below.

- The mobility and conductivity of HTM layer is critical. The HTM should have enough conductivity to minimize the series resistance, which will lead to improvement in the FF. Thus, finding a HTM with a high hole mobility and conductivity in its pristine form is important.
- It is known that the difference between the Fermi level of TiO_2 and HOMO energy level of HTM governs the V_{OC} . The focus has thus been on developing HTMs with deeper HOMO energy levels with the aim to improve the V_{OC} of the PSC. However, in most cases the PCE was only marginally improved. For example, spiro-OMeTAD, P3HT or PTAA, have comparable HOMO energy levels, but to date the best-performing devices have used spiro-OMeTAD or its derivatives. However, the chemical interactions between HTM perovskite have not yet been studied in detail. Thus, in depth understanding for the chemical interactions between perovskite and HTM is important for the rational design of efficient HTMs in the future.
- Various HTMs have been developed which show performance comparable to the state of the art spiro-OMeTAD. Some of these HTMs if not more, are equally complex to synthesize as spiro-OMeTAD. So there is a need to develop HTMs with cost-effective synthesis. Also, there is a need to develop more understanding of structure-property and device performance relationship for rational design of HTMs.
- Most of the organic small molecule HTMs used in PSCs have low mobility. This is because that most of the molecules are non-planar and not well conjugated, which leads to poor mobility. However, planar molecules, for example, acenes, which have high mobility often show poor solubility, and so cannot be used in a PSC as it is a solution processed device. Hence, the HTM should be designed so that it has good mobility and also good solubility.

- These organolead halide perovskites are susceptible towards degradation by humidity, and have stability issues under heat and light. So, the solutions to these problems can be achieved by molecular engineering of HTMs, where HTMs can protect the perovskite from humidity and UV-light-induced degradation. Moreover, the additives and dopants used in HTMs are hygroscopic in nature which can also lead to degradation of perovskite with time. Hence, it is desirable to design new HTMs which have high mobility and conductivity and so do not require additives or dopants.

2.5 Ph.D. in context of literature

In this chapter various inorganic, polymer and organic small molecule HTMs have been discussed. Spiro-OMeTAD still remains the best performing HTM. Spiro-OMeTAD has a bulky spiro core which gives it thermal stability and high T_g . Also spiro-OMeTAD has good solubility and is amorphous in nature, which gives it excellent film forming ability. At the beginning of this PhD Work, there was not much literature on alternative HTMs in PSC and most of the groups working on PSCs used spiro-OMeTAD as HTM.

The gaps in the literature which should be investigated in an attempt to develop new HTMs in a rational way have been identified and are discussed below.

- In general the HTMs consist of an aromatic or heteroaromatic core to which is attached one or more di- or tri- arylamine functional groups. Various types of cores can lead to different thermal, optical and electronic properties. Hence the correlation between the different types of cores, and the HTM and device properties should be established. The functional group used in HTMs can be linked directly to the core or electron rich groups such as a thiophene can be inserted between the core and the functional group. By making a series of related HTMs with same core but with different linkers it should be possible to elucidate the effects of such linkers on the materials and device properties

and so obtain useful structure-property relationships for rational design of HTMs.

- There exist a number of other bulky, thermally stable units similar to the spirobifluorene unit found in spiro-OMeTAD, which might be suitable as cores for HTMs. One such unit is triptycene. In addition it has not been established whether the amine unit attached to such a core should optimally be a diphenylamine as in spiro-OMeTAD, a triphenylamine or a TPA linked via a thienyl group.
- No attempts have been made to investigate furan as a possible component in HTMs in place of thiophenes. It was therefore proposed to make a HTM based on furan.
- While dithienylsilole units have been investigated the structurally related silafluorene unit has not been studied so far. It has a lower HOMO than the thienylsilole which might produce a higher V_{oc} and should be as stable.
- The role of T_g is not clear. Various molecules with different T_g are designed and their impact on the performance is discussed.
- Not much work has been done to study the charge transfer at perovskite/HTM interface, which is critical to the performance. Charge carrier dynamics and lifetime measurements have been made, employing time resolved PL to study the perovskite/HTM interface.

References

- [1] B. O'Regan, M. Grätzel, *Nature* **1991**, 353, 737-740.
- [2] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson, *Chem. Rev.* **2010**, 110, 6595-6663.
- [3] Z. Yu, F. Li, and L. Sun, *Energy Environ. Sci.* **2015**, 8, 760-775.
- [4] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, F. E. Curchod Basile, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, and M. Grätzel, *Nat. Chem.* **2014**, 6, 242-247.

- [5] S. Ahmad, E. Guillen, L. Kavan, M. Grätzel, and M. K. Nazeeruddin, *Energy Environ. Sci.* **2013**, 6, 3439-3466.
- [6] A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin, and M. Grätzel, *Science* **2011**, 334, 629-634.
- [7] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spretizer, and M. Grätzel, *Nature* **1998**, 395, 583-585.
- [8] J. Burschka, A. Dualeh, F. Kessler, E. Baranoff, N. L. Cevey-Ha, C. Yi, M. K. Nazeerudin, and M. Grätzel, *J. Am. Chem. Soc.* **2011**, 133, 18042-18045.
- [9] H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel, and N.-G. Park, *Sci. Rep.* **2012**, 2, 591(1-7).
- [10] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Science* **2012**, 338, 643-647.
- [11] M. A. Green, A. Ho-Baillie, and H. J. Snaith, *Nat. Photonics* **2014**, 8, 506-514.
- [12] S. A. Bretschneider, J. Weickert, J. A. Dorman, and L. Schmidt-Mende, *APL Mater.* **2014**, 2, 040701(1-10).
- [13] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, *J. Am. Chem. Soc.* **2009**, 131, 6050-6051.
- [14] J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park, and N.-G. Park, *Nanoscale* **2011**, 3, 4088-4093.
- [15] National Renewable Energy Laboratory Efficiency Chart <http://www.nrel.gov/ncpv/images/efficiencychart.jpg> (accessed January **2016**)
- [16] D. Bi, S.-J. Moon, L. Haggman, G. Boschloo, L. Yang, E. M. J. Johansson, M. K. Nazeeruddin, M. Grätzel, and A. Hagfeldt, *RSC Adv.* **2013**, 3, 18762-18766.

- [17] S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas, and H. J. Snaith, *J. Phys. Chem. Lett.* **2014**, 5, 4207-4212.
- [18] J. M. Ball, M. M. Lee, A. Hey, and H. J. Snaith, *Energy Environ. Sci.* **2013**, 6, 1739-1743.
- [19] G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goriely, and H. J. Snaith, *Adv. Funct. Mater.* **2014**, 24, 151-157.
- [20] D. Liu, T. L. Kelly, *Nat. Photonics* **2014**, 8, 133-138.
- [21] L. Etgar, P. Gao, Z. Xue, Q. Peng, A. K. Chandiran, B. Liu, M. K. Nazeeruddin, and M. Grätzel, *J. Am. Chem. Soc.* **2012**, 134, 17396-17399.
- [22] W. A. Laban, L. Etgar, *Energy Environ. Sci.* **2013**, 6, 3249-3253.
- [23] F. Zhang, X. Yang, H. Wang, M. Cheng, J. Zhao, and L. Sun, *ACS Appl. Mater. Interfaces* **2014**, 6, 16140-16146.
- [24] A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, M. Grätzel, and H. Han, *Science* **2014**, 345, 295-298.
- [25] J.-Y. Jeng, Y.-F. Chiang, M.-H. Lee, S.-R. Peng, T.-F. Guo, P. Chen, and T.-C. Wen, *Adv. Mater.* **2013**, 25, 3727-3732.
- [26] J.-Y. Jeng, K.-C. Chen, T.-Y. Chiang, P.-Y. Lin, T.-D. Tsai, Y.-C. Chang, T.-F. Guo, P. Chen, T.-C. Wen, and Y.-J. Hsu, *Adv. Mater.* **2014**, 26, 4107-4113.
- [27] H. Tian, B. Xu, H. Chen, E. M. J. Johansson, and G. Boschloo, *ChemSusChem* **2014**, 7, 2150-2153.
- [28] J. Qiu, Y. Qiu, K. Yan, M. Zhong, C. Mu, H. Yan, and S. Yang, *Nanoscale* **2013**, 5, 3245-3248.
- [29] H.-S. Kim, J.-W. Lee, N. Yantara, P. P. Boix, S. A. Kulkarni, S. Mhaisalkar, M. Grätzel, and N.-G. Park, *Nano Lett.* **2013**, 13, 2412-2417.
- [30] M. I. Dar, F. J. Ramos, Z. Xue, B. Liu, S. Ahmad, S. A. Shivashankar, M. K. Nazeeruddin, and M. Grätzel, *Chem. Mater.* **2014**, 26, 4675-4678.
- [31] A. Yella, L.-P. Heiniger, P. Gao, M. K. Nazeeruddin, and M. Grätzel, *Nano Lett.* **2014**, 14, 2591-2596.

- [32] X. Gao, J. Li, J. Baker, Y. Hou, D. Guan, J. Chen, and C. Yuan, *Chem. Commun.* **2014**, 50, 6368-6371.
- [33] D. Bi, G. Boschloo, S. Schwarzmuller, L. Yang, E. M. J. Johansson, and A. Hagfeldt, *Nanoscale* **2013**, 5, 11686-11691.
- [34] M. H. Kumar, N. Yantara, S. Dharani, M. Grätzel, S. Mhaisalkar, P. P. Boix, and N. Mathews, *Chem. Commun.* **2013**, 49, 11089-11091.
- [35] D.-Y. Son, J.-H. Im, H.-S. Kim, and N.-G. Park, *J. Phys. Chem. C* **2014**, 118, 16567-16573.
- [36] J.-W. Lee, D.-J. Seol, A.-N. Cho, and N.-G. Park, *Adv. Mater.* **2014**, 26, 4991-4998.
- [37] G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, and H. J. Snaith, *Energy Environ. Sci.* **2014**, 7, 982-988.
- [38] S. Pang, H. Hu, J. Zhang, S. Lv, Y. Yu, F. Wei, T. Qin, H. Xu, Z. Liu, and G. Cui, *Chem. Mater.* **2014**, 26, 14851491.
- [39] T. M. Koh, K. Fu, Y. Fang, S. Chen, T. C. Sum, N. Mathews, S. G. Mhaisalkar, P. P. Boix, and T. Baikie, *J. Phys. Chem. C* **2013**, 118, 16458-16462.
- [40] I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee, and H. I. Karunadasa, *Angew. Chem.* **2014**, 126, 11414-11417.
- [41] N. Pellet, P. Gao, G. Gregori, T.-Y. Yang, M. K. Nazeeruddin, J. Maier, and M. Grätzel, *Angew. Chem. Int. Ed.* **2014**, 53, 3151-3157.
- [42] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang, and M. G. Kanatzidis, *Nat. Photonics* **2014**, 8, 486-489.
- [43] M. H. Kumar, S. Dharani, W. L. Leong, P. P. Boix, R. R. Prabhakar, T. Baikie, C. Shi, H. Ding, R. Ramesh, M. Asta, M. Grätzel, S. G. Mhaisalkar, and N. Mathews, *Adv. Mater.* **2014**, 26, 7122-7127.
- [44] F. Hao, C. C. Stoumpos, R. P. H. Chang, and M. G. Kanatzidis, *J. Am. Chem. Soc.* **2014**, 136, 8094-8099.
- [45] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, and S. I. Seok, *Nano Lett.* **2013**, 13, 1764-1769.

- [46] N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, and S. I. Seok, *Nature***2015**, 517, 476-480.
- [47] J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, and M. Grätzel, *Nature***2013**, 499, 316-319.
- [48] M. Liu, M. B. Johnston, and H. J. Snaith, *Nature***2013**, 501, 395-398.
- [49] J.-H. Im, I.-H. Jang, N. Pellet, M. Grätzel, and N.-G. Park, *Nat. Nanotechnol.* **2014**, 9, 927-932.
- [50] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, and S. I. Seok, *Nat. Mater.***2014**, 13, 897-903.
- [51] Q. Chen, H. Zhou, Z. Hong, S. Luo, H.-S. Duan, H.-H. Wang, Y. Liu, G. Li, and Y. Yang, *J. Am. Chem. Soc.***2013**, 136, 622-625.
- [52] M. Xiao, F. Huang, W. Huang, Y. Dkhissi, Y. Zhu, J. Etheridge, A. Gray-Weale, U. Bach, Y.-B. Cheng, and L. Spiccia, *Angew. Chem. Int. Ed.***2014**, 53, 9898-9903.
- [53] F. Huang, Y. Dkhissi, W. Huang, M. Xiao, I. Benesperi, S. Rubanov, Y. Zhu, X. Lin, L. Jiang, Y. Zhou, A. Gray-Weale, J. Etheridge, C. R. McNeill, R. A. Caruso, U. Bach, L. Spiccia, and Y.-B. Cheng, *Nano Energy***2014**, 10, 10-18.
- [54] C.-W. Chen, H.-W. Kang, S.-Y. Hsiao, P.-F. Yang, K.-M. Chiang, and H.-W. Lin, *Adv. Mater.***2014**, 26, 6647-6652.
- [55] A. Marchioro, J. Teuscher, D. Friedrich, M. Kunst, R. van de Krol, T. Moehl, M. Grätzel, and J.-E. Moser, *Nat. Photonics***2014**, 8, 250-255.
- [56] (a) L. Xue-Peng, K. Fan-Tai, C. Wang-Chao, Y. Ting, G. Fu-Ling, C. Jian, D. Song-Yua, *Acta Phys.-Chim. Sin.* **2016**, 32 (6), 1347–1370. (b) Y. Shirota, H. Kageyama, *Chem. Rev.***2007**, 107, 953-1010.
- [57] J. A. Christians, R. C. M. Fung and P. V. Kamat, *J. Am. Chem. Soc.*, **2013**, 136, 758-764.
- [58] K.-C. Wang, P.-S. Shen, M.-H. Li, S. Chen, M.-W. Lin, P. Chen, and T.-F. Guo, *ACS Appl. Mater. Interfaces***2014**, 6, 11851–11858.

- [59] P. Qin, S. Tanaka, S. Ito, N. Tetreault, K. Manabe, H. Nishino, M. K. Nazeeruddin, and M. Grätzel, *Nat. Commun.***2014**, 5, 3834(1-6).
- [60] A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, and A. B. Holmes, *Chem. Rev.* **2009**, 109, 987-1091.
- [61] Y. -J. Cheng, S.-H. Yang, and C. -S. Hsu, *Chem. Rev.***2009**, 109, 5868-5923.
- [62] A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, and A. Salleo, *Chem. Rev.***2010**, 110, 3-24.
- [63] J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-J. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel, and S. I. Seok, *Nat. Photonics***2013**, 7, 486-491.
- [64] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, and S. I. Seok, *Nat. Mater.***2014**, 13, 897-903.
- [65] H. Chen, X. Pan, W. Liu, M. Cai, D. Kou, Z. Huo, X. Fang, and S. Dai, *Chem. Commun.***2013**, 49, 7277-7279.
- [66] S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas, and H. J. Snaith, *Nano Lett.* **2014**, 14, 5561-5568.
- [67] Y. Xiao, G. Han, Y. Chang, H. Zhou, M. Li, and Y. Li, *J. Power Sources***2014**, 267, 1-8.
- [68] S. Ryu, J. H. Noh, N. J. Jeon, Y. Chan Kim, W. S. Yang, J. Seo, and S. I. Seok, *Energy Environ. Sci.***2014**, 7, 2614-2618.
- [69] Y. S. Kwon, J. Lim, H.-J. Yun, Y.-H. Kim, and T. Park, *Energy Environ. Sci.***2014**, 7, 1454-1460.
- [70] Z. Zhu, Y. Bai, H. K. H. Lee, C. Mu, T. Zhang, L. Zhang, J. Wang, H. Yan, S. K. So, and S. Yang, *Adv. Funct. Mater.***2014**, 24, 7357-7365.
- [71] S. Ameen, M. S. Akhtar, H. K. Seo, and H. S. Shin, *Langmuir***2014**, 30, 12786-12794.

- [72] D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel, and A. Hagfeldt, *Sci. Adv.***2016**, 2, e1501170 (1-7).
- [73] N. J. Jeon, H. G. Lee, Y. C. Kim, J. Seo, J. H. Noh, J. Lee, and S. I. Seok, *J. Am. Chem. Soc.***2014**, 136, 7837-7840.
- [74] M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J.-P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K.-H. Dahmen, F. De Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel, and M. K. Nazeeruddin, *Nat. Energy***2016**, 1, 15017.
- [75] M. Franckevičius, A. Mishra, F. Kreuzer, J. Luo, S. M. Zakeeruddin, and M. Grätzel, *Mater. Horiz.***2015**, 2, 613-618.
- [76] P. Ganesan, K. Fu, P. Gao, I. Raabe, K. Schenk, R. Scopelliti, J. Luo, L. H. Wong, M. Grätzel, and M. K. Nazeeruddin, *Energy Environ. Sci.***2015**, 8, 1986 -1991.
- [77] Y. Shirota, *J. Mater. Chem.* 2000, 10, 1-25.
- [78] H. Li , K. Fu , P. P. Boix , L. H. Wong , A. Hagfeldt , M. Grätzel , S. G. Mhaisalkar, and A. C. Grimsdale, *ChemSusChem***2014**, 7, 3420-3425.
- [79] H. Choi, S. Paek, N. Lim, Y. H. Lee, M. K. Nazeeruddin, and J. Ko, *Chem.-Eur. J.***2014**, 20, 10894-10899.
- [80] K. Do, H. Choi, K. Lim, H. Jo, J. W. Cho, M. K. Nazeeruddin, and J. Ko, *Chem. Commun.***2014**, 50, 10971-10974.
- [81] L. Cabau, I. G. Benito, A. M. Ontoria, N. F. Montcada, N. Martin, A. V.Ferran, and E. Palomares, *Chem. Commun.***2015**, 51, 13980-13982.
- [82] P. Gratia, A. Magomedov, T. Malinauskas, M. Daskeviciene, A. Abate, S. Ahmad, M. Gr.tzel, V. Getautis, and M. K. Nazeeruddin, *Angew. Chem. Int. Ed.***2015**, 54, 11409-11413; *Angew. Chem.***2015**, 127, 11571-11575.
- [83] S. Park, J. H. Heo, C. H. Cheon, H. Kim, S. H. Im, and H. J. Son, *J. Mater. Chem. A***2015**, 3, 24215-24220.

- [84] K. Rakstys, A. Abate, M. I. Dar, P. Gao, V. Jankauskas, G. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad, M. Grätzel, and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, **2015**, 137, 16172-16178.
- [85] T. Malinauskas, M. Saliba, T. Matsui, M. Daskeviciene, S. Urnikaite, P. Gratia, R. Send, H. Wonneberger, I. Bruder, M. Graetzel, V. Getautis, and M. K. Nazeeruddin, *Energy Environ. Sci.* **2016**, 9, 1681-1686.
- [86] H. Li, K. Fu, A. Hagfeldt, M. Gratzel, S. G. Mhaisalkar, and A. C. Grimsdale, *Angew. Chem., Int. Ed.*, **2014**, 53, 4085-4088.
- [87] M. Petrus, T. Bein, T. Dingemans, and P. Docampo, *J. Mater. Chem. A* **2015**, 3, 12159-12162.
- [88] B. Xu, E. Sheibani, P. Liu, J. Zhang, H. Tian, N. Vlachopoulos, G. Boschloo, L. Kloo, A. Hagfeldt, and L. Sun, *Adv. Mater.* **2014**, 26, 6629-6634.
- [89] L. Songtao, L. Han, J. Xiao, L. Zhu, J. Shi, H. Wei, Y. Xu, J. Dong, X. Xu, D. Li, S. Wang, Y. g. Luo, Q. Meng, and X. Li, *Chem. Commun.* **2014**, 50, 6931-6934.
- [90] H. Choi, H. Jo, S. Paek, K. Ko, H. M. Ko, J. K. Lee, and J. Ko, *Chem. Asian J.* **2015**, 11, 548-554.
- [91] A. Abate, S. Paek, F. Giordano, J.-P. Correa-Baena, M. Saliba, P. Gao, T. Matsui, J. Ko, S. M. Zakeeruddin, K. H. Dahmen, A. Hagfeldt, M. Grätzel, and M. K. Nazeeruddin, *Energy Environ. Sci.* **2015**, 8, 2946-2953.
- [92] M. Manceau, F. Bundgaard, J. E. Carle, O. Hagemann, M. Helgesen, R. Sondergaard, M. Jorgensen, and F. C. Krebs, *J. Mater. Chem.* **2011**, 21, 4132-4141.
- [93] N. J. Jeon, J. Lee, J. H. Noh, M. K. Nazeeruddin, M. Grätzel and S. I. Seok, *J. Am. Chem. Soc.*, **2013**, 135, 19087-19090.
- [94] J. Liu, Y. Wu, C. Qin, X. Yang, T. Yasuda, A. Islam, K. Zhang, W. Peng, W. Chen, and L. Han, *Energy Environ. Sci.* **2014**, 7, 2963-2967.
- [95] S. Kazim, F. J. Ramos, P. Gao, M. K. Nazeeruddin, M. Grätzel, and S. Ahmad, *Energy Environ. Sci.* **2015**, 8, 1816-1823.

- [96] F. J. Ramos, K. Rakstys, S. Kazim, M. Grätzel, M. K. Nazeeruddin, and S. Ahmad, *RSC Adv.***2015**, 5, 53426-53432.
- [97] I. Lim, E.-K. Kim, S. A. Patil, D.Y. Ahn, W. Lee, N. K. Shrestha, J. K. Lee, W. K. Seok, C.-G. Choa, and S.-H. Han, *RSC Adv.***2015**, 5, 55321-55327.
- [98] H. Wang, A. D. Sheikh, Q. Feng, F. Li, Y. Chen, W. Yu, E. Alarousu, C. Ma, M. A. Haque, D. Shi, Z.-S. Wang, O. F. Mohammed, O. M. Bakr, and T. Wu, *ACS Photonics***2015**, 2, 849-855.

Chapter 3

Experimental Methodology

This chapter begins with a rationale for the choice of materials to be synthesized, and then the synthetic/purification methods will be described including their underlying principles. After that techniques used for structural, photophysical, thermal, optoelectronic and electrochemical characterization are discussed. Finally the device fabrication and testing process is discussed.

3.1 Rationale for selection of materials

Organic–inorganic metal halide perovskites, in particular methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have emerged as very promising light harvesting materials for high performance and low cost photovoltaic technology. As discussed in the previous chapter HTM play crucial in the performance of perovskite solar cells. Spiro-OMeTAD is currently the best performing HTM in PSCs, but its high cost is a serious drawback impeding its large scale application. Several other HTMs based on different design principles such as spiro-type, star shape, linear etc. have been synthesized and investigated in PSCs, but none has proved superior to spiro-OMeTAD in all aspects. The aim of the work in this thesis is to test new designs of HTMs which may show similar or better performance to spiro-OMeTAD but be more economical to make and to elucidate possible design rules for efficient HTMs.

The first design concept for a new HTM was based on triptycene. The steric bulk of triptycene (arising from the paddlewheel configuration of the three benzene rings) disrupts π – π stacking interactions, prevents efficient packing, and thus contributes to improved solubility, which is critical for solution processed devices. The bulky and twisted structure of triptycene thus has some similarity to that of spiro-OMeTAD and provides high thermal stability, and a high glass transition temperature (T_g) while the nonconjugated center keeps the triplet energy high. High solubility also makes triptycene a good candidate as a core in HTMs for solution processed devices. To study the effect of sidechains it was decided to make three triptycene derivatives with the core linked to diphenylamine groups as in spiro-OMeTAD, to TPA sidegroups as TPA moiety has easy oxidizable nitrogen atom and the ability to transport positive charges or holes, and to thienyl-TPA groups as thiophenes lower HOMO energy and also may help bind to the perovskite surface. As during the course of this study it became clear that simple linear molecules might also function as efficient HTMs, subsequent designs

focused on simple linear molecules with new core units. It was also hypothesized that such new units could also be later used in sidegroups on spirobifluorene or triptycene cores as will be discussed further in chapter 7.

Many HTMs contain thiophene groups but to date no HTM has been reported using furan which is the O-analogue of thiophene. The smaller size of the O atom in the ring compared to the S atom in thiophene based HTMs should result in closer intermolecular π - π stacking which could be beneficial for enhancing the hole transport and also increase the lifetime of charge carriers. The higher dipole moment of furan as compared to thiophene might also make furan derivatives better HTMs as there is a higher electron density on the furan O atom than on the thiophene S, which might be able to better interact with the PbI_6 octahedra. Furthermore, furan is also biodegradable and obtainable from biomass.

The third design was to use electron rich silafluorene as core. Silafluorene is a suitable core because it is planar and can have alkyl chains attached to the silicon atom to produce high solubility in organic solvents and so improve processability. Siloles are also reported to have very high photostability and may thus enhance device lifetime. Silafluorene has a silicon heteroatom and it is known that silole-containing compounds have deep HOMO levels, which is a prerequisite for achieving high V_{OC} in solar cells.

3.2 Synthesis techniques: reaction type, purification, analysis

3.2.1 Suzuki coupling

The synthesis of most of the HTMs was done via Suzuki coupling of a halogenated core and TPA boronic acid using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst, under inert atmosphere with standard solvents and bases as this reaction is a convenient and efficient aromatic C-C bond formation method [1] (Fig. 3.1). Suzuki cross-

coupling was first reported by Suzuki and Miyaura in 1979, as a palladium-catalyzed cross-coupling of organoboronic acids and organic halides or triflates. The advantages of this method are (i) mild reaction conditions, (ii) boronic acids are environmentally safer and much less toxic than the organostannanes used in Stille coupling, which is the most commonly used alternative method for aryl-aryl coupling, (iii) it is unaffected by water and has good tolerance for a wide variety of functional groups, and (iv) high stereo- and regio- selectivity. Some disadvantages include formation of self-coupling products in presence of oxygen, and side reactions such as aldol condensation due to the need to use a base. Ongoing development of the Suzuki cross-coupling includes developing advanced catalysts for unreactive aryl halides [2] and sp^3 -hybridized alkyl halides [3].

Figure 3.1 The general chemical formula for Suzuki coupling.

The catalytic cycle of the Suzuki cross-coupling includes four steps (Fig. 3.2): (i) oxidative addition of an organic halide to the $\text{Pd}(0)$ -species to form $\text{Pd}(\text{II})$, (ii) metathesis of the anion attached to the palladium for the anion of the base, (iii) transmetallation between $\text{Pd}(\text{II})$ and the alkylboronate complex, and (iv) reductive elimination to form the C-C sigma bond with regeneration of $\text{Pd}(0)$.

Figure 3.2 Catalytic cycle for Suzuki coupling

3.2.2 Column chromatography for purification of small organic molecules

Column chromatography is a technique which is used to purify small organic molecules through iterative adsorption/desorption process of the molecules between solid stationary adsorbent (stationary phase) and flowing eluent (mobile phase) [4]. Due to different adsorption affinity of different compounds with the stationary phase, different fractions of the feed can be separated and collected portionwise. Thus, it isolates desired compounds from a mixture, giving pure compounds [5].

Gravity column and flash chromatography are two sub-categories of chromatography, with the driving force for solvent flow being gravity and positive air pressure, respectively. As shown in Fig. 3.3 the process starts with placing a solid adsorbent (usually silica gel (Al_2O_3) or alumina (SiO_2)) as the stationary phase in a vertical glass column, and then adding the liquid mobile phase to the top of the adsorbent and allowing it to flow down through the column. As the eluent passes through the column, continuous equilibrium separation occurs between the solute adsorbed on the adsorbent and the solute dissolved in the eluting solvent. Various components in the mixture have different affinities

with the stationary and mobile phases, so they will be carried along with the mobile phase at different pace and separation will be done. Then individual components are collected as the solvent drips from the bottom of the column. The performance of the column chromatography is dependent on the pressure applied, the adsorbent quality, and the nature of the eluent solvent.

Large adsorbent particles (small mesh sizes) result in faster movement of the samples, and are usually used in flash chromatography for samples with few components and/or which are facile to separate. The polarity of the eluent influences the relative moving rates of the constituents in the sample mixture. With highly polar eluents, sample movement often becomes too rapid to attain any separation of the components. With weakly polar or non-polar eluents, polar compounds can become too strongly adhered to the column and cannot be eluted from the column. Hence, proper choice of an eluting solvent is crucial.

Figure 3.3 Schematic illustration of working process of column chromatography [6].

Thin-Layer Chromatography (TLC) is used to determine the separation ability of the mixture in various combinations of solvent. Usually a series of increasingly polar solvent mixtures are applied, with firstly a less-polar solvent to elute a less-polar compound, and then a more-polar solvent to elute the more-polar compound. To monitor the fractionation process, in-time analysis of column outflow is demanded. Commonly, small fractions are collected separately and their composition is rapidly analyzed by TLC and like fractions combined.

3.3 Characterization: Principles and Analysis

3.3.1 NMR spectroscopy

NMR spectroscopy is a non-destructive analytical technique, which is used for determining chemical structure, as well as purity and content of the sample [7]. In general, NMR is a phenomenon in which certain types of nuclei, depending on their spin properties, absorb and radiate electromagnetic radiation in magnetic field. The most important parameters for interpretation of NMR data are chemical shift, peaks splitting pattern, and integration value (mostly for ^1H NMR), which demonstrates the relative intensity of signals.

The chemical shift (δ) is a relative resonant frequency, which can be defined by equation:

$$\delta = \frac{\nu - \nu_s}{\nu_0}$$

Where $(\nu - \nu_s)$ is the frequency difference between the detected signal and the reference; ν_0 is the central resonant frequency for the nucleus in the applied magnetic field. In this equation, the chemical shift is a ratio of Hz to MHz, which gives a dimensionless value $1/10^6$, or ppm (parts per million). Although trimethylsilane (TMS) is a common reference for proton and carbon NMR spectroscopy, in which chemical shift is defined as zero ($\nu - \nu_s = 0$), common

solvents with known shifts can also be applied as additional internal calibration markers.

Since the effective magnetic field experienced by the nuclei depends on the degree of electron shielding around it, the chemical shift is related to the chemical environment which surrounds the nuclei. The value of the chemical shift thus depends upon the nature of neighboring atoms, including their electronic structure. Thus, substituents in organic molecules significantly influence the values of chemical shifts, as shown in Fig. 3.4 for ^1H NMR data. Electron withdrawing groups generally decrease electron density around adjacent atoms (deshielding), resulting in higher resonant frequencies of the nuclei and, thus, higher values of chemical shift. Factors related to sample preparation, such as temperature, concentration, solvent, and paramagnetic impurities can also influence chemical shift values.

Figure 3.4 Ranges of chemical shifts (δ , ppm) for ^1H in compounds with different substituents [8].

In NMR spectra, a value of chemical shift is displayed on the horizontal (x) axis, while the vertical axis represents the intensity of signals. Since relaxation times of different ^1H nuclei are generally similar, the integral ratio of different peaks is directly proportional to the quantities of different protons. Since different carbon nuclei generally have very different relaxation times, and longer relaxing nuclei give signals with lower intensity, this consideration is not usually applicable for ^{13}C spectral data.

Spin-spin coupling (also known as J-coupling) is an effect of a peak splitting into two or more lines due to the influence of adjacent nuclei on the effective magnetic field of the detected one. A ^1H NMR spectrum is a graph of resonance frequency (chemical shift) versus the intensity of RF absorption by the sample. In the first order ^1H spectra, where the difference in chemical shift is much larger than the coupling constant (measured in absolute frequency, Hertz), the total amount of lines in the peak is $N+1$, where N is number of neighboring protons of different nature in the molecule. Thus, a single line peak in ^1H NMR spectra means no adjacent protons of a different nature, two lines indicate a system with one neighboring non-identical proton, etc. A good illustration of this relation is the ^1H NMR spectra of chloroethane (Fig. 3.5), where the protons in the methylene fragment, which have three neighboring protons of different nature, appear as a quartet of four lines, and protons in the methyl group appear as a triplet of three lines. The ratio of the intensity of the signals within the mutliplets is determined by the binomial distribution (1:1 for a doublet, 1:2:1 for a triplet and so on).

Figure 3.5 ^1H NMR spectra of chloroethane [9].

In the present work, ^1H and ^{13}C NMR data were obtained on a Bruker DPX 400 MHz spectrometer (reference frequencies are 400 MHz for ^1H , 100 MHz for ^{13}C nuclei) with chemical shifts referenced to solvents like DMSO- d_6 and CDCl_3 .

3.3.2 Mass spectrometry (MALDI-TOF-MS)

Mass spectrometry (MS) is an analytical technique, which allows determination of the quantity and type of chemical species present. Mass spectra is a plot of mass-to-charge ratio versus the intensity of the peak [10]. The equipment for obtaining MS data generally consists of three main units: sample introduction system with ionization source, charged species transfer and separation system, and a detector. There are generally three steps in the working procedures for all types of MS machines, first introduction of sample to be analysed into the ionisation source to become charged species, second flight/drift of the charged species to the mass analyser, and third arrival at the detector at different places or after different times as determined by the mass/charge (m/z) ratio.

Figure 3.6 Illustration working mechanism of MALDI-TOF [11].

The operating procedure of MALDI-TOF-MS is depicted in Fig. 3.6. Application of low to medium laser power on a sample film uniformly mixed within a large amount of matrix results in heat/ionization transfer from the matrix to the sample molecules, forming differently charged ions (z is charge number) on the sample slide. A voltage gap between the sample slide and ground accelerate the ions towards the ground, with the velocity of the ions (v) governed by the law of conservation of energy ($\frac{1}{2}mv^2 = zV_0$). Then the ions start drifting towards the detector without any external drive, ions with smaller m/z value (lighter and highly charged) move faster, and the time of ion flight is indicative of different m/z .

In the present work, Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Shimadzu Biotech AXIMA-TOF.

3.3.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) [12] technique is used for measuring the thermal features of materials, by monitoring of the heat flow in the sample. In DSC the heat flow through the sample is measured against that for a reference

hollow pan, and the heat flow comparison curve can show the heat release or heat absorption peaks for the sample. The peaks are associated with different phase transformations, including melting, crystallization, glass transition, etc. Such phase changes are helpful in evaluating the proper temperature for processing the materials for various purposes. In the present work, DSC was done using TA Instrument Q10. DSC was employed for determining the T_g of the HTMs synthesized in the present study.

3.3.4 Electrochemical method: Cyclic Voltammetry

Electrochemical methods are applied to reveal oxidation/reduction changes for materials under different electrical potentials [13]. Cyclic voltammetry can be used for calculation of HOMO energy level of organic semiconductors. CV monitors the current changes as the voltage sweep goes through a common three electrode (working, counter, and reference) circuit immersed in the sample solution with an auxiliary electrolyte. A typical loop for a reversible electrochemical process is shown below, where only a single electrochemical active species exists.

Figure 3.7 Typical reversible electrochemical loops in a CV scan [14].

Oxidation at the anode takes place during the forward sweep (V_1 to V_2), and reduction on the cathode takes place during the reversed scan (Fig. 3.7). There are three criteria for a reversible electrochemical reaction as listed below:

- The voltage gap between the oxidation and reduction current peaks is only dependent on the number of electrons involved in the electrochemical process:

$$\Delta E = E_p^a - E_p^c = \frac{59}{n} \text{ mV}$$

- The value of the cathode/anode peak currents is equal or comparable:

$$\frac{i_p^a}{i_p^c} = 1$$

- The peak voltage value is independent of the scan rate, while the peak currents are proportional to the square root of the scan rate

$$i_p = (2.69 \times 10^5) n^{3/2} S D^{1/2} \nu^{1/2} C_A^* \text{ (Randles-Sevcik equation)}$$

Here, S is the surface area of the working electrode in cm^2 , n is equal to the number of electrons gained in the reduction, C_A^* is the molar concentration of A in the bulk solution, D is the diffusion coefficient and ν is the sweep rate. In the case of irreversible electrochemical reactions, usually a higher voltage is demanded to drive the reactions at a slower scanning rate, which is related to the drifting speed of active species and the change of diffusion with thickness. To sum up, CV can be used to study variety of redox processes, to determine the stability of reaction products, the presence of intermediates in redox reactions and the reversibility of a reaction.

In the present work, CV was performed to calculate the HOMO energy levels of the new HTMs. CV experiments were performed on a CHI411 electrochemical workstation. All CV measurements were recorded in dichloromethane (DCM) with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte

(scan rate = 100 mVs⁻¹). The experiments were performed at room temperature with a conventional three electrode configuration consisting of a gold counter electrode, an Ag/AgCl in 3 M KCl reference electrode and a platinum wire working electrode.

3.3.5 Ultraviolet-Visible (UV-Vis) Spectroscopy

The internal energy of a molecule of any substance is sum of the vibration energy of the constituent atoms, the rotational energy associated with the molecule and energy of its electrons. Since the electronic energy levels of a molecule are widely separated, therefore such a molecule can be excited from one energy level to another only by the absorption of a high energy photon that is, by a photon having very short wavelength [15]. When the incident light causes an electronic transition within its structure of a molecule or ion the absorption characteristics in the ultraviolet (UV, 200-400 nm) region or visible (Vis, 400-600 nm) are seen. Hence the absorption of light by a molecule in the UV or Vis region is accompanied by a transition from one molecular electronic state to another [15]. The incident photon energy promotes electrons from the ground state orbitals to higher energy excited state orbitals or antibonding orbitals. In general, there are three types of ground state orbital involved: (i) σ (bonding) molecular orbital, (ii) π (bonding) molecular orbital and (iii) n (non-bonding) atomic orbital. Apart from these three, there are two types of antibonding orbitals involved in the transition: (i) σ^* (sigma star) orbital and (ii) π^* (pi star) orbital [15]. It must be noted that there are no n^* antibonding orbitals as the n electrons do not form bonds.

In σ to σ^* transition an electron in a bonding s orbital is excited to the corresponding antibonding orbital. Similarly in π to π^* transition an electron of a lone pair is excited to an antibonding orbital [15]. Thus the possible electronic

transitions that can occur by the absorption of visible and ultraviolet light are σ to σ^* , π to π^* , n to σ^* and to π^* and as shown in Fig. 3.8.

Figure 3.8 The general pattern of energy levels and the fact that the transitions are brought about by the absorption of different amounts of energy.

The σ - σ^* and n - σ^* transitions as they require large amount of energy occur in the far-UV region or occur rather weakly in the 180-240 nm wavelength region. Due to this saturated groups do not exhibit strong absorption in the near-UV or the Vis region. The n - π^* and π - π^* transitions occur in molecules with unsaturated centers as they require less energy and occur at longer wavelengths. The π - π^* transitions, when occur in isolated groups in a molecule, give rise to absorptions of fairly low intensity [15]. However, a remarkable effect upon the absorption spectrum is seen due to the conjugation of unsaturated groups in a molecule. The wavelength of maximum absorption moves to a longer wavelength and the absorption intensity may often increase.

According to the Beer-Lambert Law [15], absorbance A is directly proportional to the path length, b , and the concentration, c , of the absorbing species

$$A = \text{Extinction Coefficient} \times \text{Cell Length} \times \text{Concentration}$$

The law is truly valid for monochromatic light or narrow band of wavelengths. Mathematically, absorbance (A) is related to percentage transmittance T by the equation:

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \log_{10} \left(\frac{100}{T} \right) = KCL.$$

Here, I_0 is the intensity of the incident light and I is the intensity of the transmitted light. The ratio I/I_0 is known as transmittance. In the above equation K, C and L are the extinction coefficient, the concentration of absorbing molecules in that path and L is the length of the radiation path through the sample. The extinction coefficient K is dependent only on the nature of the molecule and the wavelength of the incident radiation.

The spectrophotometer provides a beam of monochromatic radiation to illuminate a sample and measures I/I_0 ratio. Usually a spectrophotometer will consist of components as shown in Fig. 3.9. The incident radiation from the source is rendered monochromatic by the monochromator and allowed to pass through the sample. The intensity of light after it passes through the sample is detected and absorbance or transmittance is recorded and signal is amplified. The amplified signal is displayed with the help of computer.

Figure 3.9 Schematic diagram of a spectrophotometer.

In the present work, UV-Vis absorption spectra were recorded using a Shimadzu UV-2501PC Spectrometer and dichloromethane as used as solvent for all the molecules.

3.3.6 Time resolved photoluminescence

The charge carrier dynamics in the nanosecond regime associated with direct band gap semiconductors such as GaAs, organic, perovskite and dye sensitized systems that span the nano- to micro- second domain is studied by the time-resolved photoluminescence (TR-PL) employing time-correlated single photon counting (TCSPC). TRPL with a pulsed laser as photon source provides information about fast transitions, related to photon-molecular interactions, inter-molecular interactions, molecular-solvent interactions, etc. PL is the main data derived from this technique, which offers the opportunity for a kinetic study of various simultaneous quenching/relaxation processes, and also the average fluorescence lifetime. Direct measurement of the emission signal by photon-counting detection can afford the value of fluorescence lifetime. The schematic diagram of TR-PL components is shown in Fig. 3.10. The essential components of a set-up for measuring fluorescence lifetimes are: (i) pulsed laser source, (ii) single photon detector, (iii) monochromator or optical filters, (iv) TCSPC unit for measuring the time between excitation and fluorescence emission [16].

In the present work, Steady-state PL spectra of pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{HTM}$ film samples were recorded using a spectrofluorometer (Fluorolog, HORIBA Jobin Yvon). Time-resolved fluorescence measurements were carried out at room temperature using as excitation source the second harmonic of a titanium sapphire laser (Chameleon, Coherent Inc.) at 400 nm (100 fs, 80 MHz) and as detection Time-correlated single photon counting (TCSPC) technique with a resolution of 10 ps (PicoQuant PicoHarp 300). These

measurements were done at the School of Physical and Mathematical Sciences (SPMS), NTU by Dr. Annalisa Bruno.

Figure 3.10 Schematic diagram showing working of TR-PL set up [16].

3.3.7 Photovoltaic Measurements

The photovoltaic characteristics of the solar cells so formed were tested using a solar simulator. As the name suggests a solar simulator is a device that provides illumination the approximating natural sunlight. The purpose of the solar simulator is to replicate solar illumination in a controlled laboratory setting, the simulator should match as close as possible the AM1.5G reference spectrum, illuminate the sample uniformly and be temporally stable. A given area is exposed to solar type of energetic illumination which complies in every respect with the basic parameters of sunshine viz., intensity, spectrum, divergence, time stability and space uniformity. To this achieve this almost all the light from a

short arc xenon lamp is collected through a large number of optical channels (lenses and mirrors). The selected beams are focused and superimposed on the chosen area. The schematic diagram of solar simulator components is shown in Fig. 3.11.

Figure 3.11 Schematic diagram showing working of solar simulator [17].

In the present work the solar cells having 0.2 cm^2 active area were measured with 0.25 cm^2 metal mask using solar simulator (San-EI Electric, XEC-301S, AM 1.5, 100 mWcm^{-2}). The current-voltage data under these conditions was obtained using Keithley model 2612A source meter. Different light intensities were obtained by using UV Fused Silica Metallic Neutral Density Filters (Newport Corporation). These measurements were done at the Energy Research Institute @ NTU (ERIAN), with the assistance of Dr. Sabba Dharani.

3.4 Computational Methods

For organic hole-transporting materials (HTMs), the hole transfer can be described by the incoherent charge hopping model, in which the charge hopping rate can be approximately described by Marcus-Hush equation:

$$k_h = \frac{V_h^2}{\hbar} \sqrt{\frac{\pi}{\lambda_h k_B T}} \exp\left(-\frac{\lambda_h}{4k_B T}\right).$$

Here V_h is the electronic coupling between HOMO levels of neighbouring molecules in the HTMs crystals, T is the temperature, k_B and $\hbar$ refer to Boltzman and Planck constants. λ_h is the hole reorganization energy calculated by adiabatic potential energy surfaces method. The hole mobilities of F101 and Spiro-OMeTAD are considered to be dominated by V_h and λ_h . Electronic coupling V_{ij} , defined as $\langle \phi_i | \hat{F} | \phi_j \rangle$, can be calculated by projecting the Fock Matrix of dimer onto molecular orbitals of respective donor (ϕ_i) and acceptor molecule (ϕ_j) with the subsequent symmetric orthogonalization, where $\hat{F}$ is the Kohn-Sham Fock operator for the whole system. Then the hole mobility can be well described by the Einstein relation $\mu = \frac{eD}{k_B T}$, [18] where e is the electron charge and D is the charge diffusion coefficient of charge carriers, which can be approximately describe as $D = \frac{1}{2d} \sum_i r_i^2 k_i P_i$, where k_i and k_i are the charge-transfer rate and intermolecular distance for the dimer, and P_i represents the probability for hole hopping in the i th pathway.

The density functional theory (DFT) calculations were performed to optimize the molecular structures of molecules T101, T102, T103, S101, F101 and Spiro-OMeTAD and study their electronic and transporting properties using exchange-correlation hybrid functional B3LYP together with basis sets 6-31G(d, p). Natural transition orbitals for the main optical transitions were calculated by time-dependent DFT method. The crystal structures of S101, F101 and Spiro-OMeTAD were predicted by using the polymorph module in Material Studio.

The hybrid PBE functional and Dreiding force field were combined to predict the crystal structures. Three possible stable crystal structures with space groups $C2/c$, $P2_1/c$, and $P2_12_12_1$ for F101 and $P2_1/c$, $P2_1$, and $P2_12_12_1$ for Spiro-OMeTAD were considered in our study for the mobility calculations. All the DFT calculations were done with Gaussian09 program (Revision B.01). These calculations were performed by Dr. Jun Yin, SPMS, NTU.

3.5 Device Fabrication

PSC Devices were fabricated in ERIAN by Dr. Sabba Dharani. Fluorine doped tin oxide (FTO, <14 ohm/square, 2.2 mm thick) substrates were laser etched to form the desired pattern, which was subsequently cleaned by sonication in decon soap solution and ethanol respectively. A thin compact layer of TiO_2 acting as a blocking layer between FTO and perovskite and which is about 80 - 100 nm thick, was deposited by aerosol spray-pyrolysis, using titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol) and absolute ethanol in the ratio 1:9 by volume and ambient air was used as the carrier gas. Then these substrates were annealed at $450^\circ C$ for 30 min and then were treated with 100 mM of $TiCl_4$ solution for 60 min at $70^\circ C$, followed by rinsing with deionized water and ethanol and subsequent annealing at $500^\circ C$ for an hour. The mesoporous TiO_2 layer composed of 30-nm-sized particles was deposited by spin coating at 4,000 r.p.m. for 30 s using a commercial TiO_2 paste (Dyesol DSL 30 NRD) diluted in ethanol (2:7, weight ratio). After drying at $125^\circ C$, the TiO_2 films were gradually heated to $500^\circ C$, baked at this temperature for 15 min and cooled to room temperature. An organic-inorganic perovskite $(CH_3NH_3)PbI_3$ was deposited by sequential method [19] under controlled environment. Lead iodide (1M) was dissolved in N,N-dimethylformamide overnight under stirring conditions at $70^\circ C$ and was spincoated on the substrates at 6000 r.p.m for 5 s. These substrates were then dried for 30 mins at $70^\circ C$. Subsequently the films were dipped in 8 mg/mL solution of CH_3NH_3I in 2-propanol for 20 min and were rinsed with 2-

propanol and were spincoated at 4000 rpm for 30s for drying followed by annealing then at 100 °C for 30 min. The HTMs T101, T102, T103, F101, S101 Spiro-OMeTAD were dissolved in chlorobenzene (70 mg/ml to 100 mg/ml), respectively, and spincoated on these substrates. Additives like Li (CF₃SO₂)₂N, tert-butylpyridine and Tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) (FK 102) dopant were added to the above solution as stated in literature [19]. The masked substrates were placed in a thermal evaporator for gold (Au) deposition via shadow masking. Thickness of the Au electrode was about 100 nm and an active area of 0.2 cm² was defined by the overlap of TiO₂ and Au.

References

- [1] L. Kürti, B. Czakó. *Strategic Applications of Named Reactions inorganic Synthesis: Background and Detailed Mechanisms*; Elsevier Academic Press, 2005. ISBN: 0-12-429785-4.
- [2] (a) A. F. Littke, G. C. Fu. *Angew. Chem., Int. Ed. Engl.* **1999**, 37, 3387-3388. (b) J. P. Wolfe, R. A. Singer, B. H. Yang, and S. L. Buchwald. *J. Am. Chem. Soc.* **1999**, 121, 9550-9561.
- [3] (a) J. H. Kirchhoff, C. Dai, and G. C. Fu. *Angew. Chem., Int. Ed. Engl.* **2002**, 41, 1945-1947. (b) J. H. Kirchhoff, M. R. Netherton, I. D. Hills, and G. C. Fu. *J. Am. Chem. Soc.* **2002**, 124, 13662-13663.
- [4] <http://www.chemguide.co.uk/analysis/chromatography/column.html>
- [5] <http://orgchem.colorado.edu/Technique/Procedures/Columnchrom/Columnchrom.html>
- [6] <http://chemistry.tutorvista.com/analytical-chemistry/column-chromatography.html>
- [7] H. Günther, *NMR spectroscopy: basic principles, concepts and applications in chemistry*. 2013: John Wiley & Sons.
- [8] <http://www.cem.msu.edu/~reusch/OrgPage/nmr.html>

Chapter 4*

Novel Hole Transporting Materials Based on Triptycene Core for High Efficiency Mesoscopic Perovskite Solar Cells

A series of novel hole-transporting materials (T101, T102 and T103) based on a triptycene core have been synthesized using short routes with high yields. The optical and electrochemical properties were tuned by modifying the functional groups, through linking the triptycene to diphenylamines via phenyl and/or thienyl groups. The mesoporous perovskite solar cells fabricated using T102 and T103 as the hole transporting material (HTM) showed a power conversion efficiency (PCE) of 12.24% and 12.38%, respectively, which are comparable to that obtained using the best performing HTM spiro-OMeTAD. The T102 based device showed higher fill factor (69.1%) and V_{OC} (1.03 V) than the spiro-OMeTAD based device ($FF = 63.4\%$, $V_{OC} = 0.976$ V) whereas the T103 based device showed comparable J_{SC} (20.3 mA/cm^2) and higher V_{OC} (0.985 V) than the spiro-OMeTAD ($J_{SC} = 20.8 \text{ mA/cm}^2$) based cell.

*This section has been published substantially as “A. Krishna, D. Sabba, H. Li, Y. Jun, P. P. Boix, C. Soci, S. Mhaisalkar and A. C. Grimsdale, Novel hole transporting materials based on triptycene core for high efficiency mesoscopic perovskite solar cells”, *Chem. Sci.* **2014**, 5, 2702-2709”.

4.1 Introduction

Triptycene is the simplest member of the iptycene family, which are molecules containing three or more arene rings connected together by a [2.2.2]bicyclic bridge. Although triptycene was first prepared by Bartlett et al. in 1942, [1] research into the chemistry of triptycene has only gained significant momentum in the last decade. So far the major interests in triptycene-type molecules lie in their supramolecular chemistry, e.g., as molecular cages, ligands, coordination networks, molecular machines, etc. [2-13]. Studies on potential applications have mainly focused on areas such as molecular hosts [14], gas storage [15,16], sensors [17,18] and their use as electrophosphorescent host materials [19].

The steric bulk of triptycene (arising from the paddlewheel configuration of the three benzene rings) disrupts π - π stacking interactions, prevents efficient packing, and thus contributes to improved solubility [20], which is critical for solution processed devices. The bulky and twisted structure of triptycene has some similarity to that of spiro-OMeTAD and provides high thermal stability, and a high glass transition temperature (T_g) while the non-conjugated center keeps the triplet energy high. In organic electronics, triptycene-based materials have been used hosts for blue and other triplet emitters for high efficiency full-color OLEDs [19], but there is no report of a hole transporting material based on triptycene. High thermal stability and solubility makes triptycene a good candidate as a core in HTMs for solution processed devices.

In this chapter are reported three novel HTMs (**T101**, **T102** and **T103**) based on a triptycene central core (Fig. 4.2). All three were synthesized from a relatively inexpensive commercially available triptycene derivative in a few steps with high overall yields. In **T101** triptycene was linked to a diphenylamine derivative. In **T102**, triptycene was linked to a triphenylamine (TPA) derivative and in **T103** a thiophene was inserted between triptycene and each TPA moiety. The TPA

functional moiety is used in HTMs because of two basic properties: the easy oxidizable nitrogen atom which is stabilized by adjacent phenyl rings and the ability to transport positive charges or holes. The bulky triptycene makes the HTM thermally stable while the TPA derivatives facilitate hole transport. The optical and electrochemical properties were tuned by modifying the functional groups, through linking the triptycene to diphenylamines via phenyl and/or thienyl groups. The methoxy groups in the TPA moiety also play a key role as they help in shifting the HOMO level up and improving the solubility. In this work is investigated the performance of these three materials in perovskite solar cells as the HTMs in comparison to similar devices using spiro-OMeTAD as HTM.

Figure 4.1 Chemical structure of spiro-OMeTAD.

Figure 4.2 Chemical structures of T101, T102 and T103.

4.2 Experimental Methods

4.2.1 Synthesis

4.2.1.1 Synthesis of (4-(bis(4-methoxyphenyl)amino)phenyl)boronic acid (compound 4)

The synthesis of TPA boronic acid derivative is shown in scheme 4.1. Compound 1 and 2 were bought from Aldrich.

Scheme 4.1 Synthetic route to TPA boronic acid derivative (compound 4).

Synthesis of compound 3: compound 1 (3.2 g, 18.6 mmol), compound 2 (10 g, 42.7 mmol), KOH (6 g, 110 mmol), Cu(I)Cl (0.37 g, 0.37 mmol) and 1,10-phenanthroline (0.67 g, 0.37 mmol) were dissolved in dry and degassed toluene. The mixture was refluxed under an inert atmosphere overnight. The reaction mixture was cooled to room temperature and poured into water, extracted with dichloromethane (DCM) and the extract was washed with water. The DCM layer was dried over anhydrous MgSO_4 , concentrated under reduced pressure and the residue was purified by column chromatography on silica gel eluting with DCM:Hexane = 1:3 to obtain a white solid (5.4g, 75%).

Synthesis of compound 4: Dry compound **3** (8 g, 21 mmol) was dissolved in freshly distilled dry THF and cooled to $-70\text{ }^{\circ}\text{C}$ in dry ice under inert atmosphere, *n*-butyllithium (1.6 M in hexane) (16 mL, 25 mmol) was added dropwise. Then the reaction was warmed up to room temperature for 10 min and cooled to $-70\text{ }^{\circ}\text{C}$ again. Triisopropyl-borate (5.8 mL, 25 mmol) was added dropwise. After addition, the reaction was stirred overnight while it was gradually warmed to room temperature (RT) by allowing the dry ice to sublime. After being poured into water and the pH adjusted to 2-4 by 1M HCl, the mixture was stirred for several hours, and then extracted several times with diethyl ether. The combined ether layer was washed with water, then the diethyl ether removed and hexane (200 mL), was added. The solution was left it in a fridge overnight to allow the product to solidify and precipitate out. Upon filtration, a greenish white solid was obtained (5.8 g, 80 %) which was kept in a fridge.

4.2.1.2 Synthesis of HTMs (T101, T102 and T103)

The synthesis of **T101**, **T102** and **T103** is shown in scheme 4.2. Compound **1** was purchased from Lumtec, Taiwan. Compound **7** was bought from Aldrich.

2,6,14-Tri(N,N-bis(4-methoxyphenyl)amino)-triptycene (T101). Compound **5** (1 g, 1.58 mmol), compound **6** (1.08 g, 4.74 mmol), $t\text{BuOK}$ (1.06g, 9.48 mmol), $\text{P}(t\text{Bu})_3\text{HBF}_4$ (90 mg, 0.31 mmol) and $\text{Pd}(\text{dba})_2$ (0.18 g, 0.31 mmol) were put into a 50 mL round bottom flask (RBF) and degassed using N_2 . Dry toluene (20 mL) was degassed using N_2 and then injected into the RBF. The reaction mixture was then stirred at $80\text{ }^{\circ}\text{C}$ for 2 days. The reaction mixture was cooled to RT and toluene was removed using a rotary evaporator. The reaction mixture was then extracted with dichloromethane (DCM) and the extract was washed with water. The DCM layer was dried over anhydrous MgSO_4 , concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel

eluting with DCM/hexane=2/1 (v/v) to obtain the product as a white fluffy solid (0.85 g, 75%).

2,6,14-Tri(N,N-bis(4-methoxyphenyl)amino-phen-4-yl)-triptycene (T102).

Compound **5** (0.2 g, 0.32 mmol), compound **4** (0.39 g, 1.11 mmol), Pd(0)(PPh₃)₄ (0.12 g, 0.1 mmol), degassed toluene (20 ml) and 2 M K₂CO₃ solution (5 mL) were transferred in to a 50 mL RBF. The reaction mixture was then stirred at 80 °C under nitrogen for 1 day. The reaction mixture was cooled to r.t. and poured into water, extracted with DCM and the extract was washed with water. The DCM layer was dried over anhydrous MgSO₄, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel eluting with DCM/hexane=2/1 (v/v) to obtain the product as a white solid (0.34 g, 90%).

2,6,14-Tri(thien-2-yl)-triptycene (8). Compound **5** (1 g, 1.58 mmol), compound **7** (2.36 g, 6.33 mmol), Pd(PPh₃)₂Cl₂ (90 mg, 0.13 mmol) and degassed tetrahydrofuran (THF, 25 mL) were added into a 50 mL RBF and the reaction was stirred at 70 °C under N₂ for 12 h. The reaction solution was cooled down and the THF was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with DCM/hexane=1/3 (v/v) to obtain the product as a white solid (0.7 g, 90%).

2,6,14-Tri(5'-(N,N-bis(4-methoxyphenyl)aminophen-4-yl)thiophene-2-yl)-triptycene (T103).

Compound **8** (0.2 g, 0.4 mmol) and N-bromosuccinimide (NBS) (0.22 g, 1.23 mmol) were dissolved in freshly distilled THF (20 mL) and stirred at room temperature for 6 h under N₂. Then the solution was poured into water, stirred for few minutes and filtered. The collected white solid **9** was dried and transferred into a 50 mL RBF together with compound **4** (0.55 g, 1.2 mmol), Pd(0)(PPh₃)₄ (0.12 g, 0.1 mmol), degassed toluene (20 ml) and 2 M K₂CO₃ solution (5 mL). The reaction mixture was then stirred at 90°C under

nitrogen for 24h. The reaction mixture was cooled to room temperature and poured into water, extracted with DCM and the extract was washed with water. The DCM layer was dried over anhydrous MgSO_4 , concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel eluting with DCM/hexane=2/1 (v/v) to obtain the product T103 as a yellow solid (0.42 g, 80%).

Scheme 4.2 Synthetic route to T101–T103.

4.2.2 Quantum Chemistry Calculations

The details of the methods used are described in Chapter 3.

4.2.3 Materials and Equipment

The details of the methods used are described in Chapter 3.

4.2.4 Device Fabrication

The details of the methods used are described in Chapter 3.

4.3 Results and Discussion

4.3.1 Structural Characterization

NMR and MALDI-TOF mass spectroscopy were done to characterize the molecules.

Compound 3: White Solid, yield 70%. ^1H NMR (400 MHz CDCl_3) δ : 7.23 (d, J = 8.8 Hz), 7.03 (d, J = 8.8 Hz), 6.78-6.83 (m), 3.79 (s). ^{13}C NMR (100 MHz CDCl_3) δ : 156.7, 148.6, 141.2, 132.4, 127.2, 122.6, 115.4, 113.0, 56.1.

Figure 4.3 ^1H NMR spectrum of compound 3. Figure 4.4 ^{13}C NMR spectrum of compound 3.

Compound 4: Greenish White solid, yield 80%. ^1H NMR (400 MHz, DMSO- d_6) δ : 7.77, 7.57, 7.02 (d, J = 8.4 Hz), 6.90 (d, J = 8.4 Hz), 6.67 (d, J = 6 Hz), 3.73. ^{13}C NMR (100 MHz, DMSO- d_6) δ : 156.8, 150.9, 140.7, 136.1, 128.0, 118.3, 115.8, 56.1.

Figure 4.5 ^1H NMR spectrum of compound 4.

Figure 4.6 ^{13}C NMR spectrum of compound 4.

T101: White Solid, Yield 75%; ^1H NMR (400 MHz, CD_2Cl_2) δ : 6.92-7.10 (br, m, 18H, MeOPhH and triptyceneH), 6.81-6.84 (m, 12H, MeOPhH), 6.54 (br, 3H, triptyceneH), 5.05 (s, 1H, bridge-CH), 4.95 (s, 1H, bridge-CH), 3.79 (s, 18H, OCH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ : 156.2, 147.4, 146.9, 141.6, 126.9, 124.2, 123.9, 117.3, 117.0, 116.7, 115.0, 55.8, 52.9. HRMS (MALDI-TOF): m/z calcd for $\text{C}_{62}\text{H}_{53}\text{N}_3\text{O}_6$, 935.39; found, 935.35. Anal. calcd for $\text{C}_{62}\text{H}_{53}\text{N}_3\text{O}_6$: C, 79.55; H, 5.71; N, 4.49. Found: C, 79.36; H, 5.76; N, 4.57%. T101 structure was confirmed by ^1H NMR via proton integration and chemical shift identification. MALDI-TOF mass spectra was also consistent with the proposed structure.

Figure 4.7 ^1H NMR spectrum of T101.

Figure 4.8 ^{13}C NMR spectrum of **T101**.

T102: White Solid, yield 90%; ^1H NMR (400 MHz, CDCl_3) δ : 7.61 (br, 3H, triptyceneH), 7.44 (d, $J = 7.6$ Hz, 3H, triptyceneH), 7.28-7.35 (m, 5H, triptyceneH, PhH), 7.18-7.21 (m, 6H, PhH), 7.08 (br, 10H, PhH), 6.96 (br, 6H, PhH), 6.85 (d, $J = 8.4$ Hz, 12H, PhH), 5.54 (s, 2H, bridge-CH), 3.81 (s, 18H, OCH_3). ^{13}C NMR (100 MHz, CDCl_3) δ : 156.6, 146.4, 144.2, 141.6, 138.9, 138.5, 129.7, 128.9, 128.2, 127.2, 126.0, 124.5, 124.1, 122.8, 121.4, 115.3, 56.1, 54.8, 54.2. HRMS (MALDI-TOF); m/z calcd for $\text{C}_{80}\text{H}_{65}\text{N}_3\text{O}_6$, 1163.49; found, 1163.48. Anal. calcd for $\text{C}_{80}\text{H}_{65}\text{N}_3\text{O}_6$: C, 82.52; H, 5.63; N, 3.61. Found: C, 82.38; H, 5.66; N, 3.64%. T102 structure was confirmed by ^1H NMR via proton integration and chemical shift identification. MALDI-TOF mass spectra was also consistent with the proposed structure.

Figure 4.9 ^1H NMR spectrum of T102.

Figure 4.10 ^{13}C NMR spectrum of **T102**.

Compound 4: White solid, Yield 90 %; ^1H NMR (400 MHz, CDCl_3) δ : 7.68 (s, 3H, triptyceneH), 7.66 (s, 3H, triptyceneH), 7.41-7.44 (m, 3H, triptyceneH), 7.22-7.29 (m, 6H, ThH), 7.02-7.04 (m, 3H, ThH), 5.51 (s, 1H, bridge-CH), 5.49 (s, 1H, bridge-CH). ^{13}C NMR (100 MHz, CDCl_3) δ : 146.1, 145.0, 144.6, 132.5, 128.5, 125.2, 124.8, 124.7, 123.9, 123.8, 123.6, 122.4, 122.3, 54.4, 54.0. HRMS (MALDI-TOF): m/z calcd for $\text{C}_{32}\text{H}_{20}\text{S}_3$, 500.07; found, 500.04.

T103: Yellow Solid, yield 80%; ^1H NMR (CD_2Cl_2) δ : 7.72 (d, $J = 5.2$ Hz, 3H, triptyceneH), 7.34-7.48 (m, 9H, PhH, triptyceneH), 7.32 (d, $J = 7.6$ Hz, 3H, triptyceneH), 7.25 (d, $J = 3.6$ Hz, 3H, ThH), 7.16 (d, $J = 3.6$ Hz, 3H, ThH), 7.09 (d, $J = 8.8$ Hz, 12H, PhH), 6.86-6.92 (m, 18H, PhH), 5.56 (s, 1H, bridge-CH), 5.54 (s, 1H, bridge-CH), 3.81 (s, 18H, OCH_3). ^{13}C NMR (CD_2Cl_2) δ : 156.7, 148.8, 146.0, 144.3, 144.0, 142.4, 140.9, 132.3, 131.3, 127.2, 126.59, 126.55, 124.49, 124.40, 122.9, 121.4, 121.3, 120.6, 115.1, 68.2, 65.9, 55.9. HRMS (MALDI-TOF): m/z calcd for $\text{C}_{92}\text{H}_{71}\text{N}_3\text{O}_6\text{S}_3$, 1410.45; found, 1410.46. Anal. calcd for $\text{C}_{92}\text{H}_{71}\text{N}_3\text{O}_6\text{S}_3$: C, 78.33; H, 5.07; N, 2.98; S, 6.82. Found: C, 78.25; H, 5.05; N, 3.09; S, 6.77%. T103 structure was confirmed by ^1H NMR via proton integration and chemical shift identification. MALDI-TOF mass spectra was also consistent with the proposed structure.

Figure 4.13 ^1H NMR spectrum of T103.

Figure 4.14 ^{13}C NMR spectrum of **T103**.

4.3.2 Modeling and Quantum Chemistry Calculations

The electronic and optical properties of triptycene-based materials were predicted by using quantum chemistry calculations performed by Dr J. Yun at SPMS, NTU. The purpose of DFT calculations is to obtain energy change trends and gain insight into how organic terminal/functional groups can tune these energy levels. As shown in Fig.4.15 and Table 4.1, the LUMO energies of **T101**, **T102** and **T103** decrease successively from **T101** to **T103** with little shift in HOMO levels upon enlarging the molecular conjugated length using linking groups between central triptycene and terminal diphenylamine group (benzene for **T102**, benzene and thiophene for **T103**). It is well known that DFT can underestimate the HOMO and LUMO energy levels [21,22]. Hence the calculated absolute value could be different from the experimental value, but the trends of

calculated HOMO, LUMO levels and ionization potentials usually match well those seen in the experimental data. Similar to the case of spiro-OMeTAD [23], HOMOs of triptycene-based materials are delocalized over the whole molecule. By contrast the LUMOs are largely localized on the diphenylamine units in **T101** or on linking groups in **T102** and **T103**, which is unlike the LUMO of spiro-OMeTAD which is localized on the central spiro-group. Here, the resulting partial wave function overlap between LUMO and HOMO leads to a strong Coulombic interaction, which can explain the favored formation of neutral excitons and enhance hole transport. The calculated hole reorganization energies (λ_{hole}) of these triptycene-based materials (80-120 meV) are much smaller than typical hole-transporting spiro-OMeTAD (148 meV) meaning that **T101**, **T102** and **T103** can be anticipated to be good hole-transporting materials in perovskite-based solar cells.

Figure 4.15 Calculated and experimental ionization potential (IP), HOMO, LUMO levels and electronic density distributions of Spiro-OMeTAD and triptycene-based HTMs T101, T102 and T103.

The calculated and experimental absorption spectra of triptycene-based materials are shown in Fig. 4.16. The CAM-B3LYP method is well-known to overestimate the excitation energy but gives results that are closer to experimental data than hybrid GGA functional such as B3LYP. Despite the discrepancies between the experimental and calculated values the TD-DFT calculations do help to illustrate the trends in spectral maxima and can help to interpret the fundamental absorption peak as an electronic transition, where the individual excited states can be further analyzed using natural transition orbitals (NTOs), [24,25] giving a simple orbital picture of the results of TD-DFT calculations by representing each electronic transition in terms of two orbitals (electron and hole). The transition carries the largest oscillator strength leading to the high-energy absorption band in these hole transporting materials, which constitutes the lowest-energy absorption band in the experimental spectrum. The corresponding dominant NTOs clearly show its significant charge-transfer (CT) character with the central triptycene unit acting as an electron acceptor for given optical transitions from the ground to excited states. In calculated absorption spectra, we can see the trend of the shift of the absorption spectra in HTMs T101-T103. In going from T101 to T103 the conjugation is increased by inserting π -linkers in between the core and the functional group which leads to the red shift in the absorption spectra. This trend of absorption shift coincides well with the experimental spectra. This kind of simulation can very useful to see the effect of insertion of the π -linker on the conjugation and can help to choose the correct π -linkers.

Figure 4.16 Calculated and experimental absorption spectra (in dichloromethane) of triptycene-based materials (**T101**, **T102** and **T103**).

Table 4.1 Summary of the calculated optical and electronic properties.

Molecule	LUMO (eV)	HOMO (eV)	-IP ^a (eV)	E _g ^b (eV)	λ _{hole} (meV)	λ _{electron} (meV)
Spiro-OMeTAD	-0.61	-4.21	-5.01	3.72	148	334
T101	-0.52	-4.60	-5.19	4.17	119	112
T102	-0.94	-4.75	-5.23	3.99	83	328
T103	-1.22	-4.51	-5.11	3.43	87	333

^a ionization potential (IP) calculated by total energy difference of $E_{\text{cation}} - E_{\text{neutral}}$, ^b $S^0 \rightarrow S^1$ excitation energy determined by the TDDFT/CAM-B3LYP method.

4.3.3 Thermal, optical and electrochemical properties

The UV-Vis absorption spectra of **T101**, **T102** and **T103** are shown in Fig. 4.16. **T101**, **T102** and **T103** exhibit absorption peak centered at 305, 340 and 390 nm, respectively. The spectra of **T102** and **T103** are red shifted as compared to **T101**, which can be attributed to the increase in π -conjugation. In **T102** π -conjugation is extended by inserting a phenyl ring between the triptycene and diphenylamine moieties which is further extended in **T103** by inserting thienyl

groups. The optical band gap (E_g) can be calculated from the absorption onset wavelength of the corresponding absorption spectrum. **T101**, **T102**, **T103** and spiro-OMeTAD are 381, 400, 458 and 420 nm, respectively which correspond to optical band gaps (E_g) of 3.25, 3.1, 2.71 and 2.98 eV for **T101**, **T102**, **T103** and **spiro-OMeTAD**, respectively.

Cyclic voltammograms of **T101**, **T102**, and **T103** are shown in Fig. 4.17. The pair of redox peaks for all the HTMs is reversible, showing that they have excellent electrochemical stability. The HOMO energy level was calculated from the CV data using the following equation: $E_{\text{HOMO}} = -5.1 - (E_{\text{ox,HTM}} \text{ vs Fc/Fc}^+)$ (eV), where $E_{\text{ox,HTM}} \text{ vs Fc/Fc}^+$ is the onset of oxidation potential with reference to ferrocene [26]. The HOMO levels of **T101**, **T102** and **T103** calculated from CV are -5.29, -5.35 and -5.33 eV, respectively. The HOMO energy level reported for perovskite is - 5.44 eV [27], which indicates that all the HTMs have energetics favorable for hole transfer (Fig. 4.18b). Table 4.2 summarizes the optical and electrochemical properties of the three HTMs. Spiro-OMeTAD has HOMO of - 5.2 eV which is higher as compared to the triptycene derivatives. As the difference between the Fermi level of TiO_2 and HOMO of HTM determines open circuit voltage (V_{oc}), a higher V_{oc} is expected for all the HTMs especially **T102**. The measured DSC results were plotted in Figure 4.17 (b).

DSC data shows high T_g of 120, 140 and 108 °C for **T101**, **T102** and **T103**, respectively; while the T_g of spiro-OMeTAD is reported to be 120 °C [28]. The T_g values among the three triptycenes varied significantly, which can be attributed to the subtle interplay between the twisted bulky side groups and the rigid triptycene core. Cross-section SEM picture (Fig. 4.18a), shows the formation of a well-defined multilayered structure with clear interfaces. The thicknesses of the TiO_2 , perovskite and the HTM layers are ~320, 200 and 250 nm, respectively.

Table 4.2 Summary of the experimental optical and electronic properties.

Molecule	$\lambda_{\max}$ (nm)	$E_{\text{opt.gap}}^a$ (eV)	LUMO ^b (eV)	HOMO (eV)
Spiro-OMeTAD	385	2.98	-2.24	-5.22
T101	302	3.25	-2.04	-5.29
T102	340	3.10	-2.25	-5.35
T103	388	2.71	-2.62	-5.33

^aOptical gap determined from UV absorption onset, ^b $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{opt.gap}}$.

Figure 4.17 (a) Cyclic Voltammograms of Spiro-OMeTAD, T101, T102 and T103 with ferrocene as the reference; (b) Differential Scanning Calorimetry (DSC) curves of T101, T102 and T103.

Figure 4.18 (a) Cross-sectional SEM of the device using T103 as HTM; (b) band diagram for the device with HTMs T101, T102, T103 and spiro-OMeTAD.

4.3.3 Device performance

The cross-section of the PSC device and energy band diagram for the device with the three HTMs and spiro-OMeTAD is shown in Fig. 4.19 (a).

Figure 4.19 (a) Current density vs. voltage curve; (b) IPCE spectra of the perovskite solar cell devices with T101, T102 T103 and Spiro-OMeTAD as HTM, respectively.

The PCE of the device with **T101**, **T102**, **T103** and spiro-OMeTAD as HTM were 8.42%, 12.24%, 12.38% and 12.87%, respectively. The device fabricated without HTM shows PCE of only 4.69%, which confirms that an HTM must be an integral component of the device for obtaining high PCE. The short circuit current (J_{sc}) of the cells fabricated from **T101**, **T102**, **T103** and spiro-OMeTAD are 13.5, 17.2, 20.3 and 20.8 mA/cm², respectively. The J_{sc} are well matched with the integrated J_{sc} obtained from integrated photo conversion efficiency (IPCE) spectra as shown in Fig. 4.19 (b) and also show similar trends. The similar shapes of the IPCEs for all the samples suggest that HTM absorption has negligible effect on the device performance. Impedance spectroscopy was performed on the spiro-OMeTAD, **T102** and **T103** based devices by Dr Pablo P. Boix at ERI@N, in order to elucidate the differences in their working mechanisms. The fitting of the results followed previous models employed in perovskite solar cells, wherein the high frequency part of the impedance spectrum is attributed to the hole transport in the HTM, whereas the resistance of the lower frequency feature is determined by the recombination process [29,30]. The maximum splitting of the Fermi levels for photogenerated electrons and holes

defines the V_{OC} . As a result, it is determined by the energetics (in our case, the different positions of the HTMs HOMO), the amount of photogenerated charge and the recombination. For both **T102** and **T103** based devices, the obtained V_{oc} are slightly higher than those of spiro-OMeTAD-based device. The device using **T102**, presents similar recombination resistance to the spiro-OMeTAD device (Fig. 4.20a), which should not make a difference in the achieved potential. Additionally, it has lower charge generation, as can be inferred from the lower J_{SC} , and ~ 130 meV deeper HOMO. These opposing factors result in a higher V_{OC} for the solar cells with the novel material.

The case of **T103** is different: although the solar cells based on this material present similar charge generation (i.e. photocurrent) to the spiro-OMeTAD-based one, the ~ 110 meV extra potential expected from the HOMO level shift is not reflected in the cell performance. The cause for this can be found in the recombination of the devices. Fig. 4.20a shows the recombination resistance of the devices, where the higher recombination for **T103** device is clear.

Another remarkable difference in the performance is the higher fill factor higher for the **T102** device. The fill factor can be explained on the basis of series resistances (Fig. 4.20b) and recombination (Fig. 4.20a), which were studied by means of impedance spectroscopy. The devices with **T102** have lower HTM resistance than **T103** and spiro-OMeTAD ones, which explains the higher fill factor achieved by these samples. Whereas the HTM resistances of **T103** and spiro-OMeTAD are similar, the higher recombination of the **T103** device results in a slightly lower fill factor. The major characteristics of the PSC devices incorporating **T101**, **T102**, **T103** and spiro-OMeTAD as HTMs are summarized in table 4.3.

Table 4.3 Summary of device various parameters; current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), efficiency (η). Champion cell data is given in parentheses. Average data with standard deviation were based on ten cells.

HTM	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (η) %
Spiro-OMeTAD	20.13±0.61 (20.8)	0.98±0.018 (0.976)	62.4±1.36 (63.4)	12.3±0.28 (12.87)
T101	13.2±0.31 (13.5)	1±0.010 (0.996)	62.67±0.42 (62.6)	8.31±0.08 (8.42)
T102	16.87±0.39 (17.2)	1.037±0.007 (1.03)	68.08±0.9 (69.1)	11.91±0.29 (12.24)
T103	20.15±0.21 (20.3)	0.981±0.007 (0.985)	62.04±1.28 (61.9)	12.26±0.06 (12.38)
Without HTM	10.6	0.844	52.5	4.7

Figure 4.20 (a) Recombination resistance and (b) Transport resistance of HTMs in the full solar cell determined by electrochemical impedance spectroscopy.

4.4 Conclusion and Outcomes

In summary, a series of novel HTMs based on triptycene core has been designed and synthesized. HTMs **T102** and **T103** exhibit extended conjugation, which facilitated by insertion of phenyl ring between the triptycene and diphenylamine moieties in **T102** and thienyl group in **T103**. All the three HTMs have high T_g and thermal stability. When used as HTM in perovskite solar cells these showed very promising performance as compared to the most widely used spiro-OMeTAD, while offering much simpler synthesis and potentially much lower production cost. Devices fabricated from **T102** and **T103** show PCE of 12.24 and 12.34 %, respectively which are comparable to that of the spiro-OMeTAD based device (PCE =12.87%). **T101** based devices showed considerably lower PCE of 8.34%. These results show that the performance of these three materials was profoundly influenced by the sidechains. Impedance spectroscopy was done to elucidate the difference in the performance of device with different HTMs. The PSC device with **T102** presents similar recombination resistance to spiro-OMeTAD device, while the one with **T103** as HTM shows higher charge recombination for device. This results in a lower FF for the device with **T103** as HTM. So far all the conditions were based on those applied to spiro-OMeTAD. One can be confident that further optimization of parameters such as film thickness, customized TiO_2 paste, solvent, heat treatment and dopant (kind and concentration) could further boost the performance of the device. The exciting finding of triptycene as high performance HTMs for PSCs opens new avenues in the design and synthesis of HTMs for PSCs. The results obtained from these HTMs show that the choice of functional sidegroup and/or linker has major effects on device performance thus helping to establish design principles for high performance HTMs. Thienyltriphenylamine groups gave the best results. Hence the nature of the core and side chains must be taken into consideration while designing a new HTM for high efficiency PSCs.

References

- [1] P. D. Bartlett, M. J. Ryan, and S. G. Cohen. *J Am. Chem. Soc.***1942**, 64, 2649-2653.
- [2] X.-Z. Zhu, C.-F. Chen. *J. Am. Chem. Soc.***2005**, 127, 13158-13159.
- [3] T. Han, C.-F. Chen, *Org. Lett.***2006**, 8, 1069-1072.
- [4] J. H Chong, M. J. MacLachlan. *J. Org. Chem.***2007**, 72, 8683-8690.
- [5] C. Zhang, C.-F. Chen. *J. Org. Chem.***2007**, 72, 9339-9341.
- [6] C. E. Godinez, G. Zepeda, and M. A. Garcia-Garibay, *J. Am. Chem. Soc.***2002**, 124, 4701-4707.
- [7] T. R. Kelly, J. P. Sestelo, and I. Tellitu, *J. Org. Chem.* **1998**, 63, 3655-3665.
- [8] T. R. Kelly, M. C. Bowyer, K. V. Bhaskar, D. Bebbington, A. Garcia, F. Lang, M. H. Kim, and M. P. Jette. *J. Am. Chem. Soc.***1994**, 116, 3657-3658.
- [9] K. Nikitin, H. Müller-Bunz, Y. Ortin, W. Risse, and M. J. McGlinchey, *Eur. J. Org. Chem.***2008**, 18, 3079-3084.
- [10] T. Han, C.-F. Chen. *J. Org. Chem.* **2007**, 72, 7287-7293.
- [11] X.-X. Peng, H.-Y. Lu, T. Han, and C.-F. Chen, *Org. Lett.* **2007**, 9, 895-898.
- [12] F. Akutsu, G. Saito, M. Miyamoto, Y. Kasashima, M. Inoki, and K. Naruchi, *Macromol. Chem. Phys.* **1996**, 197, 2239-2245.
- [13] J. Lu, J. Zhang, X. Shen, D. M. Ho, and R. A. Pascal. *J. Am. Chem. Soc.***2002**, 124, 8035-8041.
- [14] S. W. Thomas, T. M. Long, B. D. Pate, S. R. Kline, E. L. Thomas, and T. M. Swager, *J. Am. Chem. Soc.***2005**, 127, 17976-17977.
- [15] B. S. Ghanem, M. Hashem, K. D. M. Harris, K. J. Msayib, M. Xu, P. M. Budd, N. Chaukura, D. Book, S. Tedds, A. Walton, and N. B. McKeown, *Macromolecules***2010**, 43, 5287-5294.

- [16] J. H. Chong, S. J. Ardakani, K. J. Smith and M. J. MacLachlan, *Chem. Eur. J.* **2009**, 15, 11824-11828.
- [17] D. Zhao, T. M. Swager, *Macromolecules* **2005**, 38, 9377-9384.
- [18] T. M. Swager, *Acc. Chem. Res.* **2008**, 41, 1181-1189.
- [19] H.-H. Chou, H.-H. Shih, and C.-H. Cheng, *J. Mater. Chem.* **2010**, 20, 798-805.
- [20] S. Mondal, S. Chakraborty, S. Bhowmick, and N. Das, *Macromolecules* **2013**, 46, 6824-6831.
- [21] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett* **2004**, 393 (1-3), 51-57.
- [22] K. Rakstys, A. Abate, M. I. Dar, P. Gao, V. Jankauskas, G. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad, M. Grätzel, and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, **2015**, 137 (51), 6172-16178.
- [23] S. Fantacci, F. D. Angelis, M. K. Nazeeruddin, and M. Gratzel, *J. Phys Chem. C* **2011**, 115, 23126-23133.
- [24] R. L. Martin, *J. Chem. Phys.* **2003**, 118, 4775-4777.
- [25] R. Tautz, E. Da Como, C. Wiebeler, G. Soavi, I. Dumsch, N. Frohlich, G. Grancini, S. Allard, U. Scherf, G. Cerullo, S. Schumacher, and J. Feldmann, *J. Am. Chem. Soc.* **2013**, 135, 4282-4290.
- [26] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, and G. C. Bazan, *Adv. Mater.* **2011**, 23, 2367-2371.
- [27] J. Burschka, N. Pellet, S. J. Moon, R. H. Baker, P. Gao, M. K. Nazeeruddin, and M. Grätzel, *Nature*, **2013**, 499, 316-319.
- [28] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spretizer, and M. Grätzel, *Nature* **1998**, 395, 583-585.
- [29] A. Dualeh, T. Moehl, N. Tétreault, J. Teuscher, P. Gao, M. K. Nazeeruddin, and M. Grätzel, *ACS Nano* **2013**, 8, 362-373.
- [30] V. Gonzalez-Pedro, E. J. Juárez-Pérez, W. S. Arsyad, E. M. Barea, F. Fabregat-Santiago, I. Mora-Sero, and J. Bisquert, *Nano Lett.*, **2014**, 14, 888-893.

Chapter 5*

Facile Synthesis of a Furan–Arylamine Hole-Transporting Material for High-Efficiency Mesoscopic Perovskite Solar Cells

*A novel hole-conducting molecule (**F101**) based on a furan core has been synthesized via a short route with high yield. When used in mesoporous methylammonium lead halide perovskite solar cells (PSCs) as the hole transporting material (HTM) it produced high power conversion efficiency (PCE) of 13.2%, which was higher than the efficiency obtained using the commonly used HTM spiro-OMeTAD (13%). The **F101**HTM based device exhibited a higher J_{SC} of 19.63 mA/cm² and a remarkably high V_{OC} of 1.1V while the spiro-OMeTAD based device demonstrated a J_{SC} ~18.4 mA/cm² and V_{OC} of 1.05V. The steady state and time resolved photoluminescence show that **F101** has significant charge quenching ability. The simple molecular structure, straight forward high yielding synthesis and higher performance in devices makes **F101** an excellent candidate for replacing the expensive spiro-OMeTAD as HTM in PSCs.*

*This section has been published substantially as “A. Krishna, D. Sabba, Y. Jun, A. Bruno, P. P. Boix, H. A. Devi, G. Yang, G. G. Gurzadyan, C. Soci, S. Mhaisalkar, and A. C. Grimsdale, *Facile Synthesis of a Furan-Arylamine Hole Transporting Material for High Efficiency Mesoscopic Perovskite Solar Cells*, *Chem. Eur. J.* **2015**, 21 (43), 15113-15117”.

5.1 Introduction

Discovered in 1870, [1] furan is the one of the simplest heteroaromatic compounds. Compared to furan, the thiophene-based materials have been much more studied and have attracted tremendous attention in organic electronics. Recently, furans were used on organic dyes for DSSC and have emerged as an alternative to thiophenes. The devices with furan based materials have shown very similar optical and electronic properties to those using the thiophene analogues [2,3]. Walker et al. [4] introduced furan-based heterocycles as peripheral substituents in one of the highest performing organic small molecules for OPV. The lack of studies on polymer backbones containing furans is surprising, given the fact that furans exhibit comparable degree of aromaticity and have similar energy levels relative to their thiophene counterparts [5,6]. Also the smaller size of the heteroatom (O vs. S) means they should show closer packing and thus potentially better charge transport. Unlike thiophene or acene-based materials, furan can be obtained entirely from natural renewable resources (such as D-xylose), hence, it falls into the category of renewable and sustainable synthetic resources [7]. In fact, furfural, a chief furan precursor, was first manufactured industrially by the Quaker Oats company in 1922 from bio-waste [8]. In addition, unlike most other building blocks of organic electronic materials, furan and many furan-based derivatives are biodegradable [9]. It has also been reported that the solubility of oligofurans is significantly better than that of the corresponding oligothiophenes [10].

In this chapter, is reported a novel HTM F101 containing an electron rich furan core linked to triphenyl amine (TPA) moieties. As mentioned above, the smaller size of the O atom in the ring compared to S in similar previously reported thiophene based HTMs [11,12] should result in closer intermolecular π - π stacking which could be beneficial for enhancing the hole transport and also increase the lifetime of charge carriers. Furthermore, the small molecular size of the HTM could lead to better pore filling of the mesoporous TiO₂ layer. The

structure of F101 is shown in Fig. 5.1. F101 was synthesized from a relatively inexpensive commercially available furan derivative in a single step with high yield and has high solubility in common organic solvents. The performance of F101 in mesoscopic perovskite solar cells has been investigated. The devices fabricated using F101 outperformed the state-of-the-art HTM spiro-OMeTAD, showing efficiencies over 13% with a remarkably high open circuit voltage of 1.1V.

Figure 5.1 Chemical structures of F101.

5.2 Experimental

Various experimental stages are described in detailed in the following subsections.

5.2.1 Synthesis

The synthesis route of F101 is very much shorter and less expensive as compared to spiro-OMeTAD (scheme 5.1). The commercially available relatively inexpensive 2,5-dibromofuran was Suzuki coupled with a triphenylamine boronic acid derivative to give F101 with high yield as shown in scheme 5.1.

Synthesis of TPA derivative: As described in Chapter 4.

Synthesis of 4,4'-(furan-2,5-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (F01). 2,5-Dibromofuran (0.25 g, 1.12 mmol), {4-[bis(4-methoxyphenyl)amino]phenyl} boronic-acid (0.825 g, 2.35 mmol), Pd(0)(PPh₃)₄ (0.13 g, 0.1 mmol), K₂CO₃ (5 mL) and degassed toluene (20 ml) were transferred to a 50 mL round bottle flask (RBF). This reaction mixture in RBF was then stirred at 90°C under nitrogen for 48 h. The reaction mixture was cooled to room temperature and poured into water, extracted with DCM and washed with water. The DCM layer was dried over MgSO₄, concentrated and the residue mixture was purified by column chromatography on silica gel eluting with DCM/hexane=3/2 (v/v) to obtain the product as a yellow solid (0.48 g, 65 %). The F101 has melting point of 147°C.

Scheme 5.1 Synthetic route for F101.

5.2.2 Computational Methods

The details of the methods used are described in Chapter 3.

5.2.3 Materials and Equipment

The details of the methods used are described in Chapter 3.

5.2.4 Device Fabrication

The details of the methods used are described in Chapter 3.

5.3 Results and Discussions

5.3.1 Structural Characterization

MALDI-TOF mass spectroscopy (Fig 5.4), ^1H NMR (Fig. 5.2) and ^{13}C NMR (Fig. 5.3) were performed to characterize F101.

F101: Yellow solid, yield 65%; ^1H NMR (DMSO- d_6 , 400 MHz, 298K): δ : 7.594 (d, $J=8.8$ Hz, 4H, PhH), 7.082 (d, $J=8.8$, 8H, PhH), 6.968 (d, $J=8.8$ Hz, 8H, PhH), 6.851 (d, $J=8.8$ Hz, 4H, PhH), 6.811 (s, 2H, furan H), 3.781 (s, 12H, OCH₃). ^{13}C NMR (DMSO- d_6 , 100 MHz, 298K): δ : 156.72, 153.08, 140.79, 127.55, 125.21, 123.31, 120.40, 115.89, 107.04, 56.15. HRMS (MALDI-TOF): m/z calcd. for C₄₄H₃₈N₂O₅, 674.80; found, 674.05. F101 structure was confirmed by ^1H NMR via proton integration and chemical shift identification. MALDI-TOF mass spectra was also consistent with the proposed structure.

Figure 5.2 ^1H NMR spectrum of F101.

Figure 5.3 ^{13}C NMR spectrum of F101.

Figure 5.4 MALDI-TOF mass spectra of F101.

5.3.2 Quantum Calculations

This section describes the theoretically estimated structural and electronic properties of F101.

Figure 5.5 (a) Chemical Structure of F101, electronic density distribution of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for F101; (b) Chemical Structure of Spiro-OMeTAD, electronic density distribution of LUMO and HOMO for Spiro-OMeTAD.

In the molecular design of hole transporting materials (HTM), the heteroatom (such as group XVI atoms) are used in the building block to adjust HOMO and LUMO levels, while the hole-accepting ability of the material is produced by the N atoms of diphenylamine [14]. The calculated HOMO level (-4.23 eV) of F101 by DFT/B3LYP method is slightly higher than that of spiro-OMeTAD (-4.48 eV), which could facilitate better hole transfer between F101 and the perovskite. The hole mobility of F101 was evaluated and compared with spiro-OMeTAD (Table 5.1 and 5.2) based on different transfer pathways in the predicted crystal structures as shown in Fig. 5.6 and Fig. 5.7. Although the calculated hole reorganization energy of F101 (227 meV) is larger than that of spiro-OMeTAD (148 meV), the resulting hole mobilities of F101 (2.61, 0.044 and 0.055 cm²/V·s) for the three possible crystal structures are higher than those of spiro-OMeTAD (0.0065, 0.0063 and 0.0845 cm²/V·s). This is due to the larger electronic coupling achieved in F101 crystals, especially under face-to-face dimer configuration (pathway 4 of C2/c space group) with effective π -orbital overlap, showing that F101 is quite promising HTM with relatively high mobility. In a previous study it has been demonstrated that the interaction between terminal methoxybenzene groups (CH₃OC₆H₅) of Spiro-OMeTAD and CH₃NH₃PbI₃ is important for efficient hole transfer, especially on the preferred (001) and (110) surfaces [15]. So F101 has four anchored terminal methoxybenzene groups for enhanced hole transport. From the electron density distribution diagrams, it is observed that the electronic cloud of F101 delocalizes over the whole molecule in the HOMO (Fig 5.5a) while for the LUMO, it is mainly localized on the central furan and benzene units (Fig 5.5a). Thus, the planar central units of F101 play a dual role in PSCs: (1) they enhance the electronic cloud overlapping between HOMO of F101 and valence band maximum of CH₃NH₃PbI₃, (2) they improve the hole transporting mobility due to large electronic coupling between F101 molecules at short intermolecular distances.

Figure 5.6 Different hole transfer pathways for possible crystal structures (a) C2/C, (b) P21/c and (c) P212121 of F101 molecule.

Table 5.1 Intermolecular electronic coupling, distance and transfer rate and hole mobility of F101 crystal.

Crystal Structure	Pathway	Electronic Coupling (meV)	Distance (Å)	Charge Transfer Rate (s^{-1})	Mobility ($cm^2/V \cdot s$)
C2/C	1	21.79	9.77	1.84×10^{12}	2.61
	2	7.76	13.67	2.33×10^{11}	
	3	0.88	22.22	3.00×10^9	
	4	91.21	11.52	3.22×10^{13}	
	5	0.92	13.89	3.25×10^9	
P21/c	1	14.77	9.08	8.45×10^{11}	0.044
	2	0.34	13.43	4.45×10^8	
	3	2.47	13.07	2.36×10^{10}	
P212121	1	17.27	8.71	1.16×10^{12}	0.055
	2	0.10	15.79	3.97×10^7	
	3	2.64	11.33	2.71×10^{10}

Figure 5.7 Different hole transfer pathways for possible crystal structure (a) P21/c, (b) P21 and (c) P212121 of spiro-OMeTAD molecule.

Table 5.2 Intermolecular electronic coupling, distance and transfer rate and hole mobility of spiro-OMeTAD crystal.

Crystal Structure	Pathway	Electronic Coupling (meV)	Distance (Å)	Hole Transfer Rate (s ⁻¹)	Mobility (cm ² /V·s)
P21/c	1	1.27	17.15	1.66×10^{10}	0.0065
	2	2.05	15.24	4.35×10^{10}	
	3	2.10	16.00	4.56×10^{10}	
P21	1	1.07	16.02	1.19×10^{10}	0.0063
	2	2.47	13.67	6.43×10^{10}	
	3	0.81	16.30	6.78×10^9	
P212121	1	2.75	15.52	7.84×10^{10}	0.0845
	2	9.73	11.92	9.80×10^{11}	
	3	0.41	14.88	1.78×10^9	

5.3.3 Optoelectronic and electrochemical properties

The opto-electronic properties of F101 have been investigated systematically and discussed in detail in the following.

Figure 5.8 (a) Absorption Spectra for spiro-OMeTAD and F101 (dichloromethane as solvent); (b) Cyclic voltammogram for spiro-OMeTAD and F101; (c) Band diagram for the device with new HTM F101 and spiro-OMeTAD and (d) Cross-sectionnal SEM image of device fabricated with F101.

From the UV-Vis absorption spectra (shown in Fig. 5.8a), it observed that F101 and spiro-OMeTAD showed absorption peak centered at 393 nm and 385 nm, respectively i.e., the absorption maxima of F101 is slightly red shifted compared to spiro-OMeTAD. This suggests there is better conjugation in F101 than in

spiro-OMeTAD. It is observed that the absorption onset wavelengths of F101 and spiro-OMeTAD are 446 nm and 425 nm, which correspond to optical band gaps of 2.78 eV and 2.92 eV, respectively.

Cyclic voltammograms of F101 and spiro-OMeTAD are shown in Fig. 5.8(b). The pair of redox peaks for F101 is highly reversible, showing that it has excellent electrochemical stability. The HOMO energy level was calculated from the CV data using the following equation: $E_{\text{HOMO}} = -5.1 - (E_{\text{ox,HTM vs. Fc/Fc}^+})$ (eV), where $E_{\text{ox,HTM vs. Fc/Fc}^+}$ is the onset of oxidation potential of ferrocene, which is used as reference and -5.1 eV is the redox potential of ferrocene [16]. The HOMO levels of F101 and spiro-OMeTAD as calculated from CV are 5.18 eV and 5.19 eV, respectively. For $\text{CH}_3\text{NH}_3\text{PbI}_3$ the reported HOMO energy level is 5.44 eV [17], which indicates that F101 has favorable energetics for the hole transfer (Fig. 5.8c). The energetics of the system employing the F101/spiro-OMeTAD are represented in (Fig 5.8c). The difference between the Fermi level of TiO_2 and HOMO of HTM is one of the factors for determining open circuit voltage (V_{OC}) of the cell [18,19], so a similar V_{OC} is expected for both F101 and spiro-OMeTAD. Table 5.3 summarizes the optical and electrochemical properties of the two HTMs.

The cross-sectional scanning electron microscopy (SEM) images shown in the Fig. 5.8d show the formation of a well-defined hybrid structure with clear interfaces. The thicknesses of the TiO_2 , perovskite and the HTM layers were ~300, 260 and 190 nm, respectively. To investigate the charge-carrier mobility of F101 and spiro-OMeTAD, field effect transistors (FETs) were fabricated. Hole mobilities evaluated from FET transfer characteristics (shown in Fig. 5.9) are $1.2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (at $V_{\text{d}} = -50 \text{ V}$; $V_{\text{g}} = -40 \text{ V}$) for spiro-OMeTAD, and $1.1 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (at $V_{\text{d}} = -50 \text{ V}$; $V_{\text{g}} = -40 \text{ V}$) for F101. Spiro-OMeTAD thus has a slightly higher field-effect mobility than F101. The simulations suggested F101 could have a higher mobility than spiro-OMeTAD. Indeed the estimated

value was high enough to open the possibility of pristine F101 being usable as dopant free HTM. However, since simulations were done using an ideal organic crystal obtained from a dimer model they tend to overestimate the mobility and when the actual mobility was measured it was discovered that in thin films F101 has a low mobility similar to that of spiro-OMeTAD which could be because factors like quality of films, defect in films, and also device fabrication expertise. This suggests that a dopant such as FK102 is required for doping F101.

Table 5.3 Optical, and electrochemical properties of F101 and spiro-OMeTAD.

HTM	$\lambda_{\max}$ (nm)	λ_{onset} (nm)	$^a E_g$ (eV)	E_{HOM} o (eV)	$^b E_{\text{LUM}}$ o (eV)	$^c \mu_h$ (cm ² /Vs)
F101	393	446	2.78	-5.18	-2.4	1.1×10^{-4}
Spiro-OMeTAD	385	425	2.92	-5.19	-2.27	2×10^{-4}

[a] Optical band gap (E_g) obtained from the onset value of absorption (λ_{onset}). [b] LUMO calculated by LUMO = HOMO + E_g . [c] Field effect hole mobility.

Figure 5.9 Transfer characteristics in the p-channel type FET of (a) spiro-OMeTAD and (b) F101. These characteristics were measured at $V_g = -40V$.

5.3.4 Device Performance

The current–density–voltage (J–V) characteristics of the devices employing F101 and spiro-OMeTAD as HTMs, together with a device without HTM are shown in Fig. 5.10a and summarized in Table 5.4. The PCE of the best performing device with F101 and spiro-OMeTAD as HTM were 13.2%, and 13.0%, respectively. The best performing device fabricated without HTM had a PCE of only 5.2%, which confirms that an HTM is a vital component of high efficiency perovskite solar cells. The short circuit current densities (J_{sc}) of the cells fabricated using F101 and spiro-OMeTAD are 19.63 mA/cm² and 18.4 mA/cm², respectively.

Figure 5.10 Current density vs. voltage curve under AM 1.5G illumination (100 mW/cm²); (b) recombination resistance extracted from fitting of the EIS results under illumination for perovskite solar cells with F101 and Spiro-OMeTAD as the HTM.

Table 5.4 Summary of device parameters; open circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and efficiency (η). Champion cell data is given in parentheses. Average data with standard deviation were based on ten cells.

HTM	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	FF (%)	PCE
F101	19.65 ± 0.039 (19.63)	1.1 ± 0.0007 (1.1)	60.02 ± 0.48 (61)	13.0 ± 0.09 (13.12)
Spiro-OMeTAD	17.6 ± 0.92 (18.4)	10.37 ± 0.016 (1.05)	67.48 ± 0.38 67.2	12.3 ± 0.74 (13.0)
W/O HTM	9.58	0.7	77.5	5.2

Figure 5.11 IPCE spectra of the device with HTMs F101 and Spiro-OMeTAD.

The J_{sc} values obtained from the IV measurements are in close agreement with the J_{sc} integrated from the IPCE spectra (Fig 5.11). The higher J_{sc} in devices with F101, may be because of higher the HOMO level of F101 provides higher driving force which could facilitate better charge injection. Also the devices with F101 showed a higher open circuit voltage ($V_{oc}=1.1\text{V}$) than devices employing spiro-OMeTAD. The V_{oc} depends on two factors; (1) the maximum splitting of the

Fermi levels for photogenerated electrons and holes and (2) the recombination of the photogenerated charges [18,19]. However, from the CV data, it can be observed that the HOMO energy levels for F101 and spiro-OMeTAD are similar; indeed the higher HOMO of F101 would be expected to produce a lower V_{OC} . Hence the origin of V_{OC} enhancement in case of F101 HTM based devices can be only explained in terms of the charge recombination process. Consequently, to understand and elucidate the process of recombination, electrochemical impedance spectroscopy was carried out. The fitting of the impedance results (R_{ct} vs applied voltage as shown Fig. 5.10b) followed previous models employed in perovskites solar cells, where the resistance of the lower frequency feature is determined by the recombination process [20-22]. In Fig. 5.10b, it is evident that F101 based devices exhibited higher resistance to charge recombination in comparison to spiro-OMeTAD, which is attributed to its planar structure coupled with efficient π - π stacking which assists in faster hole transport thereby reducing voltage losses. However, the high device performance of F101 is limited by the poor fill factor ($FF= 0.61$) which is attributed to a high series resistance of the device as calculated from J-V curve. In contrast the spiro-OMeTAD based devices exhibited better FF (0.67) because of lower series resistance. This shortcoming in F101 devices can be improved by further optimization of the HTM over layer thickness [23,24]. If the FF could be improved to match that of the spiro-OMeTAD the efficiency would be $\sim 1.3\%$ higher.

5.3.5 Steady State and Time-resolved PL

To further look in to the charge-carrier dynamics and separation at the perovskite/HTM interface, steady state photoluminescence (PL) and time resolved PL quenching were studied. The PL investigations establish the occurrence of an efficient charge extraction at the perovskite/HTM.

Figure 5.12 (a) The steady-state photoluminescence (PL) spectra and (b) Time-resolved PL spectra of CH₃NH₃PbI₃, CH₃NH₃PbI₃/Spiro-OMeTAD and CH₃NH₃PbI₃/F101.

From the steady state PL spectra (recorded by Dr. Annalisa Bruno at SPMS), shown in Fig. 5.12a, it is evident that both HTMs significantly quench perovskite emission signal, with HTM F101 having slightly better PL quenching efficiency, ~ 97%, compared to ~ 93% for spiro-OMeTAD. To get insights in to the life of the charge-carrier and to prove the dynamic charge separation, time resolved PL measurements were carried out (by Dr Annalisa Bruno at SPMS) by monitoring the emission peak at 760nm (Fig. 5.12b) after excitation at 400 nm. The pristine perovskite exhibited a life time (τ_{av}) of ~ 2.6 ns, whereas it decreased in bilayer samples (CH₃NH₃PbI₃/HTM). Both HTMs spiro-OMeTAD and F101 showed a similar decay lifetime of τ_{av} ~ 1 ns. This proves that charge pairs generated upon illumination in perovskite are efficiently separated at the perovskite/HTM interface and then transferred to the HTM. It can thus be concluded that F101 and spiro-OMeTAD show comparable quenching ability.

Table 5.5 Time resolved photoluminescence characterization of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. The data were collected at the maximum of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite emission (760 nm).

Sample	τ_1 (ns)	Fraction	τ_2 (ns)	Fraction	τ_{av} (ns)
$\text{CH}_3\text{NH}_3\text{PbI}_3$	3.3	0.68	0.9	0.32	2.6
$\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro}$	1.8	0.40	0.4	0.6	1
$\text{CH}_3\text{NH}_3\text{PbI}_3/\text{F101}$	2.2	0.24	0.7	0.76	1

5.4 Conclusions and Outcome

A novel HTM F101 based on a furan core has been designed, synthesized and used in PSCs. The new HTM F101 outperforms most widely used state of the art HTM spiro-OMeTAD while offering simpler and economical synthesis route. This is the first reported on furan based HTM for PSCs. Its good charge injection properties enabling high current densities ($J_{\text{SC}}=19.63 \text{ mA/cm}^2$) and better charge recombination resistance assisting in attainment of high V_{OC} (1.1V), resulting in PCE >13%, which is slightly higher than the spiro-OMeTAD based devices obtained in the present study. The interfacial charge separation (at the perovskite/HTM interface) efficiency of F101 is found to be comparable to be that of the spiro-OMeTAD. The charge carrier dynamics and lifetime results show that F101 has excellent hole quenching ability. It is likely that with further optimization and fine tuning of various device parameters and by developing more understanding of interfacial characteristics, there can be significant enhancement in the device performance. Simple molecular structure, straight forward synthesis with high yields with possibility of easy up-scalability and high performance gives F101 a great potential to replace the more expensive spiro-OMeTAD. The results also suggest that furans should be further investigated as replacements for thiophene units in HTMs.

References

- [1] H. Limpricht, *Ber. Dtsch. Chem. Ges.* **1870**, 3, 90-91.
- [2] R. Z. Li, X. J. Lv, D. Shi, D. F. Zhou, Y. M. Cheng, G. L. Zhang, and P. Wang, *J. Phys. Chem. C* **2009**, 113, 7469-7479.
- [3] J. T Lin, P. C. Chen, Y. S. Yen, Y. C. Hsu, H. H. Chou, and M. C.P. Yeh. *Org. Lett.* **2009**, 11, 97-100.
- [4] B. Walker, A. B. Tomayo, X. D. Dang, P. Zalar, J. H. Seo, A. Garcia, M. Tantiwiwat, and T. Q. Nguyen, *Adv. Funct. Mater.* **2009**, 19, 3063-3069.
- [5] U. H. F. Bunz, *Angew. Chem., Int. Ed.* **2010**, 49, 5037-5040.
- [6] Z. F. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, and P. V. Schleyer, *Chem. Rev.* **2005**, 105, 3842-3888.
- [7] a) M. N. Belgacem, A. Gandini, *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, **2008**, Chap. 6; b) A. Gandini, *Macromolecules* **2008**, 41, 9491-9504; c) J. B. Binder, and R. T. Ronald, *J. Am. Chem. Soc.* **2009**, 131, 1979-1985; d) A. Gandini, *Green Chem.* **2011**, 13, 1061-1083.
- [8] H. E. Hoydonckx, W. M. Van Rhijn, W. Van Rhijn, D. E. De Vos, and P. A. Jacobs in *Ullmanns Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2000**.
- [9] a) M. Okada, K. Tachikawa, and K. Aoi, *J. Appl. Polym. Sci.* **1999**, 74, 3342-3350; b) F. Koopman, N. Wierckx, J. H. de Winde, and H. J. Ruijsenaars, *Proc. Natl. Acad. Sci.(USA)* **2010**, 107, 4919-4924; c) A. Gandini, *ACS Symp. Ser.* **1990**, 433, 195-208.
- [10] O. Gidron, M. Bendikov, *Angew. Chem. Int. Ed.* **2014**, 53, 2546-2555.
- [11] H. Li, K. Fu, A. Hagfeldt, M. Grätzel, S. G. Mhaisalkar, and A. C. Grimsdale, *Angew. Chem., Int. Ed.* **2014**, 53, 4085-4088.

- [12] T. Krishnamoorthy, K. Fu, P. P. Boix, H. Li, T. M. Koh, W. L. Leong, S. Powar, A. C. Grimsdale, M. Grätzel, N. Mathews, and S. G. Mhaisalkar, *J. Mater. Chem. A* **2014**, 2, 6305-6309.
- [13] J. Burschka, N. Pellet, S. J. Moon, R. H. Baker, P. Gao, M. K. Nazeeruddin, and M. Grätzel, *Nature*, **2013**, 499, 316-319.
- [14] J. Yin, S. L. Zhang, R. F. Chen, Q.D. Ling, and W. Huang, *Phys. Chem. Chem. Phys.* **2010**, 12, 15448-15458.
- [15] J. Yin, D. Cortecchia, A. Krishna, S. Chen, N. Mathews, A. C. Grimsdale, and C. Soci, *J. Phys. Chem. Lett.* **2015**, 6, 1396-1402.
- [16] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, and G. C. Bazan, *Adv. Mater.* **2011**, 23, 2367-2371.
- [17] H. Kim, J. H. Im, C. R. Lee, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. H. Baker, J. H. Yum, J. E. Moser, M. Grätzel, and N. G. Park, *Sci. Rep.* **2012**, 2, 591(1-7).
- [18] N. J. Jeon, J. Lee, J. H. Noh, M. H. Nazeeruddin, M. Grätzel, and S. I. Seok, *J. Am. Chem. Soc.* **2013**, 135, 19087-19090.
- [19] A. Krishna, D. Sabba, H. Li, J. Yin, P. P. Boix, C. Soci, S. G. Mhaisalkar, and A. C. Grimsdale, *Chem. Sci.*, **2014**, 5, 2702-2709.
- [20] A. Dualeh, T. Moehl, N. Tetreault, J. Teuscher, P. Gao, M. K. Nazeeruddin, and M. Grätzel, *ACS Nano* **2014**, 8, 362-373.
- [21] V. Gonzalez-Pedro, E. J. Juarez-Perez, W. S. Arsyad, E. M. Barea, F. Fabregat Santiago, I. Mora-Sero, and J. Bisquert, *Nano Lett.* **2014**, 14, 888-893.
- [22] H.-S. Kim, J.-W. Lee, N. Yantara, P. P. Boix, S. A. Kulkarni, S. Mhaisalkar, M. Grätzel, and N.-G. Park, *Nano Lett.* **2013**, 13, 2412-2417.
- [23] N. Marinova, W. Tress, R. Humphry-Baker, M. I. Dar, V. Bojinov, S. M. Zakeeruddin, M. K. Nazeeruddin, and M. Grätzel, *ACS Nano* **2015**, 9, 4200-4209.
- [24] Q. Wang, C. Bi, and J. Huang, *Nano Energy* **2015**, 15, 275-280.

Chapter 6*

Facile Synthesis of Hole Transporting Material with Silafluorene Core for Efficient Mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells

A novel electron-rich small-molecule, 4,4'-(5,5-dihexyl-5H-dibenzo[b,d]silole-3,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline (S101), containing silafluorene as core with arylamine side groups, has been synthesized via a short efficient route. When incorporated into a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cell as a hole transporting material (HTM), a short circuit photocurrent density (J_{sc}) of $18.9\text{mA}/\text{cm}^2$, an open circuit voltage (V_{oc}) of 0.92 V, a fill factor (FF) of 0.65 contributing to an overall power conversion efficiency (PCE) of ~11% was obtained which is comparable to the PCE obtained using the current state-of-the-art HTM 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) ($\eta=12.3\%$). S101 is thus a promising HTM with the potential to replace the expensive spiro-OMeTAD due to its comparable performance and much simpler and less expensive synthesis route.

*This section has been published substantially as “A. Krishna, D. Sabba, Y. Jun, A. Bruno, L. J. Antila, C. Soci, S. Mhaisalkar and A. C. Grimsdale, *Facile Synthesis of Hole Transporting Material with Silafluorene Core for Efficient Mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells*, *J. Mater. Chem. A* **2016**, 4, 8750-8754.

6.1 Introduction

It has been proved that the bridging atoms in cyclic units on the main chain of conjugated polymers can greatly influence the properties of the materials [1-6]. For example, it has been reported that the crystallinity of silole-containing materials is significantly better as compared to their carbon-bridged analogues, which results in a better charge transport and might be also responsible for the reduced bimolecular recombination which can boost the device performance [7]. Silole and its derivatives have been widely used in organic electronics because of their excellent properties like deep HOMO level, good redox stability in air and high charge carrier mobility [1,8-11].

In this chapter is reported, a novel HTM S101 (Fig. 6.1) based on an electron rich silafluorene core to which are linked hole-accepting triphenylamine moieties while hexyl chains are attached to the silicon atom to produce high solubility in organic solvents and so improve solution processing. The S101 molecule has a planar structure which is desirable for promoting intramolecular π -delocalization and intermolecular π - π stacking, which favor both charge carrier mobility and lifetime, boosting device efficiency [11]. Silafluorene based materials have been used in efficient organic light emitting diodes [12]. S101 was synthesized from a relatively inexpensive commercially available silafluorene derivative in a single step with an acceptable yield (45%). In addition to extensive investigation of its material properties, e.g., structural, thermal, electrochemical and optoelectronic characteristics, the performance of S101 in mesoscopic perovskite solar cells has been investigated. For this the detailed photo-electrical characteristics and steady state and time resolved PL investigations have been performed.

Figure 6.1 Chemical structures of F101.

6.2 Experimental

6.2.1 Synthesis

The synthesis route of S101 is shorter and less expensive as compared to spiro-OMeTAD (see Scheme 6.1). The commercially available relatively inexpensive 3,7-dibromo-5,5-dihexyl-5H-dibenzo[b,d]silole (Lumtec, Taiwan) was Suzuki coupled with a triphenylamine boronic acid derivative to give S101 in 45% yield from an unoptimised reaction.

Scheme 6.1 Synthetic route for S101.

Synthesis of TPA derivative: Detailed synthesis of TPA is described in Chapter 4.

Synthesis of 4,4'-(5,5-dihexyl-5H-dibenzo[b,d]silole-3,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline (S101). 3,7-Dibromo-5,5-dihexyl-5H-dibenzo-[b,d]-silole (0.8 g, 1.58 mmol), {4-[bis(4-methoxyphenyl)amino]phenyl} boronic-acid (1.16g g, 3.3 mmol), Pd(0)(PPh₃)₄ (0.13 g, 0.1 mmol), K₂CO₃ (5 mL) and degassed toluene (20 ml) were transferred in to a 50 mL round bottle flask (RBF). This reaction mixture in RBF was then stirred at 90°C under nitrogen for 48 h. The reaction mixture was cooled to RT and poured into water, extracted with dichloromethane (DCM) and the extract was washed with water. The DCM layer was dried over MgSO₄, concentrated and the residue mixture was purified by column chromatography on silica gel eluting with DCM/hexane=1/1 (v/v) to obtain the product as a white solid (0.68 g, 45 %). S101 has melting point of 143°C.

6.2.2 Materials and Equipment

The details of the methods used are described in Chapter 3.

6.2.3 Device Fabrication

The details of the methods used are described in Chapter 3.

6.2.4 Computational Methods

The details of the methods used are described in Chapter 3.

6.3 Results and Discussions

6.3.1 Structural Characterization

MALDI-TOF mass spectroscopy, ^1H and ^{13}C NMR was performed to characterize the HTM.

S101: Yellow Solid, Yield 45%; ^1H -NMR (CDCl_3 , 400 MHz): δ (ppm): 7.86 (d, 2H, $J=8\text{Hz}$, PhH), 7.80(d, 2H, $J=1.6\text{Hz}$, PhH), 7.63 (dd, 2H, $J=8.2\text{ Hz}$, PhH), 7.50 (d, 4H, $J=8\text{Hz}$, PhH), 7.12 (d, 8H, $J=8\text{Hz}$, PhH), 7.04 (d, 4H, $J=8\text{Hz}$, PhH), 6.87 (d, 8H, $J=8\text{Hz}$, PhH), 3.82 (s, 12H, OCH_3), 1.42 (m, 4H, C_6H_{13} H), 1.29 (m, 4H, C_6H_{13} H), 1.22 (m, 8H, C_6H_{13} H), 0.99 (m, 4H, C_6H_{13} H), 0.83 (t, 6H, $J=6.8\text{Hz}$, C_6H_{13} H). ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm): 155.99, 148.16, 146.79, 141.13, 139.42, 138.71, 133.44, 131.34, 128.46, 127.55, 126.66, 121.17, 121.08, 114.86, 55.65, 33.23, 31.49, 24.08, 22.70, 14.20, 12.56. HRMS (MALDI-TOF): m/z calcd for $\text{C}_{64}\text{H}_{68}\text{N}_2\text{O}_4\text{Si}$, 957.34; found, 957.00. S101 structure was confirmed by ^1H NMR via proton integration and chemical shift identification. MALDI-TOF mass spectra was also consistent with the proposed structure.

Figure 6.3 ^{13}C NMR spectrum of S101.

Figure 6.4 MALDI-TOF mass spectrum of S101.

6.3.2 Quantum Calculations

Figure 6.5 (a) Chemical structure of S101, electronic density distribution of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for S101; (b) chemical structure of spiro-OMeTAD, electronic density distribution of LUMO and HOMO for spiro-OMeTAD.

Fig. 6.5 shows the chemical structure of the S101 and spiro-OMeTAD together with the electronic density distribution of their frontier orbitals calculated by density functional theory (DFT). For S101, the highest occupied molecular orbital (HOMO) level shows π -bonding character, spreading over the whole molecule; while the lowest unoccupied molecular orbital (LUMO) shows π^* -antibonding character being predominately localized on the central silafluorene and two benzene units. The calculated HOMO energy of S101 (-4.49 eV) is quite

close to that of spiro-OMeTAD (-4.48 eV), which would promote effective hole transfer from perovskite to S101.

The hole transfer rate of hole-transporting materials can be described by the Marcus-Hush equation which is dominated by two important parameters, namely, (1) reorganization energy and (2) electronic coupling, which can be obtained from DFT calculations. Fig. 6.6 demonstrates the predicted crystal structures of S101 and spiro-OMeTAD with all possible hole-hopping pathways. The molecular structure of S101, with a planar silafluorene core, has much smaller intermolecular distances, resulting in larger electronic coupling between HOMO levels of neighboring molecules, which can improve the hole transporting mobility (see Table 6.1 and 6.2). S101 shows smaller hole reorganization energy (0.13 eV) than spiro-OMeTAD (0.15 eV) and the predicted hole mobility for the simulated charge transport pathways (0.215, 0.141, and 0.049 cm²/V.s) are one order of magnitude higher than those of spiro-OMeTAD (0.0058, 0.0046, and 0.0532 cm²/V.s). These values are comparable with the high performing furan-based HTM F101 discussed in the previous chapter [14], showing that S101 could also be a promising HTM with potentially relatively high hole mobility.

Figure 6.6 (a) Hole transfer pathways for possible crystal structure (1) C2/c, (2) P/1 and (3) P212121 of S101; (b) hole transfer pathways for possible crystal structure (1) C2/c, (2) P21 and (3) P212121 of spiro-OMeTAD.

Table 6.1 Intermolecular electronic coupling, distance and transfer rate and hole mobility of S101 crystal (Fig 6.6a).

Crystals	Pathway	Electronic Coupling (meV)	Distance(Å)	Hole Transfer Rate (s ⁻¹)	Mobility (cm ² /V·s)
C2/c	1	3.18	8.56750	1.05×10^{11}	0.215
	2	27.5	6.68700	7.81×10^{12}	
	3	5.85	10.86821	3.54×10^{11}	
P/1	1	26.2	5.73052	7.11×10^{12}	0.141
	2	4.91	6.34593	2.49×10^{11}	
	3	5.67	10.81330	3.33×10^{11}	
P212121	1	12.0	7.08085	1.49×10^{12}	0.049
	2	0.25	13.65105	6.50×10^8	
	3	0.51	10.72813	2.68×10^9	

Table 6.2 Intermolecular electronic coupling, distance and transfer rate and hole mobility of Spiro-OMeTAD crystal (Fig 6.6b).

Crystals	Pathway	Electronic Coupling (meV)	Distance (Å)	Hole Transfer Rate (s ⁻¹)	Mobility (cm ² /V·s)
C2/C	1	1.13	17.15	1.32×10 ¹⁰	0.0058
	2	1.99	15.24	4.10×10 ¹⁰	
	3	1.96	16.00	3.96×10 ¹⁰	
P21	1	0.95	16.02	9.38×10 ⁹	0.0046
	2	2.08	13.67	4.48×10 ¹⁰	
	3	0.45	16.30	2.14×10 ⁹	
P212121	1	2.67	15.52	7.36×10 ¹⁰	0.0532
	2	7.80	11.92	6.30×10 ¹¹	
	3	0.11	14.88	1.26×10 ⁸	

6.3.3 Thermal, optical and electrochemical properties

The optoelectronic properties of S101 have been systematically investigated and compared with those of spiro-OMeTAD. In the UV-Vis absorption spectra (shown in Fig. 6.7a), absorption peaks of S101 and spiro-OMeTAD were observed at 381 nm and 384 nm, respectively. The absorption onset wavelengths of S101 and spiro-OMeTAD are 434 nm and 420 nm, respectively which correspond to band gaps of 2.86 eV and 2.95 eV, respectively. The onset of absorption in S101 is slightly red shifted with respect to spiro-OMeTAD which can be attributed to the more extended conjugation in the backbone of S101 due to the presence of two extra phenyl rings between the nitrogen atoms.

From the cyclic voltammograms of S101 and spiro-OMeTAD, shown in Fig. 6.7b, the pair of redox peaks for S101 is observed to be highly reversible, showing that it has excellent electrochemical stability. The HOMO energy level

was calculated from the CV data using the following equation: $E_{\text{HOMO}} = -5.1 - (E_{\text{ox,HTM}} \text{ vs. Fc/Fc}^+) \text{ (eV)}$, where $E_{\text{ox,HTM}} \text{ vs. Fc/Fc}^+$ is the onset of oxidation potential of ferrocene, which is used as reference and -5.1 eV is the redox potential of ferrocene [15]. The HOMO levels of S101 and spiro-OMeTAD as calculated from CV are 5.33 eV and 5.15 eV, respectively while the reported HOMO energy level of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is 5.44 eV [16] which indicates that the new HTM S101 has favorable energetics for the hole transfer (Fig. 6.7c). The energetics of the system employing S101/spiro-OMeTAD is represented in Fig. 6.7d and Table 6.3 summarizes the optical and electrochemical properties of the two HTMs.

Differential scanning calorimetry (DSC) showed S101 has a weak glass transition (T_g) at 45 °C and a melting point (T_m) of 143 °C (see Fig. 6.8). The glass transition and melting temperature of spiro-OMeTAD are $T_g = 124$ °C and $T_m = 245$ °C, respectively.

The cross-sectional scanning electron microscopy (SEM) images shown in Fig. 6.7d display the various interfaces of the S101 HTM based $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cell indicating we have achieved formation of a well-defined hybrid structure with clear interfaces. From the FE-SEM image the thicknesses of the TiO_2 , perovskite and the HTM layers can be estimated to be ~350, 550 and 200 nm, respectively.

To investigate the charge-carrier mobility of S101 and spiro-OMeTAD, field effect transistors (FETs) were fabricated. Hole mobilities evaluated from FET transfer characteristics (Fig. 6.9) are $2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (at $V_d = -50 \text{ V}$; $V_g = -40 \text{ V}$) for spiro-OMeTAD, and $7.2 \times 10^{-5} \text{ cm}^2/\text{Vs}$ (at $V_d = -50 \text{ V}$; $V_g = -40 \text{ V}$) for S101. Spiro-OMeTAD thus has a slightly higher field-effect mobility than S101. The simulations suggested S101 should have a higher mobility than spiro-OMeTAD. Indeed the estimated value was high enough to open the possibility of pristine

S101 being usable as a dopant free HTM. However, since simulations were done using an ideal organic crystal obtained from a dimer model, they tend to overestimate the properties and when the devices are fabricated to measure actual mobility it turned out the HTM in thin films has a low mobility similar to that of spiro-OMeTAD which could be because factors like quality of films, defect in films, and also device fabrication expertise. This suggests that dopant like FK102 is required for doping S101.

Figure 6.7 (a) Absorption spectra for spiro-OMeTAD and S101 (Dichloromethane as solvent), (b) cyclic voltammograms for spiro-OMeTAD and S101, c) band diagram for the device with new HTM S101 and spiro-OMeTAD, and d) cross-sectional SEM image of device fabricated with S101.

Table 6.3 Thermal, optical and electrochemical properties of S101 and spiro-OMeTAD.

HTM	λ_{max} (nm)	λ_{onset} (nm)	E_g (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	T_g (°C)	μ_h (cm ² /Vs)
S101	381	434	2.86	-5.32	-2.46	45	7.2×10^{-5}
Spiro-OMeTAD	384	420	2.95	-5.15	-2.2	124	2×10^{-4}

Figure 6.8 Differential Scanning Calorimetry (DSC) curves for S101.

Figure 6.9 Transfer characteristics in the p-channel type FET of (a) spiro-OMeTAD and (b) S101. These characteristics are measured at $V_g = -40V$.

6.3.4 Device Performance

The current–voltage (J–V) characteristics of perovskite solar cells employing S101 and spiro-OMeTAD as HTMs, together with devices without HTM are shown in Fig. 6.10 and obtained device parameters are summarized in Table 6.4. The PCEs of the best performing device with S101 and spiro-OMeTAD as HTM are 11% and 12.3% respectively. This study also showed that the device fabricated without the HTM had a PCE of only around 4.7 %, which confirmed that a HTM must be an integral component of the high efficiency perovskite solar cells. The short circuit current densities (J_{SC}) of the cells fabricated using spiro-OMeTAD and S101 are 19.7 mA/cm^2 and 18.9 mA/cm^2 , respectively. The slightly higher current using spiro-OMeTAD can be attributed to its higher HOMO level as compared to S101, which gives spiro-OMeTAD a higher driving force for charge transfer from the perovskite to the HTM. The devices fabricated from both HTMs exhibit similar fill factors. The devices with S101 showed a slightly lower open circuit voltage ($V_{\text{OC}} = 0.92V$) than devices employing spiro-OMeTAD ($V_{\text{OC}} = 0.975V$). However, from the CV data, it can be seen that the HOMO energy level for S101 is deeper than for spiro-OMeTAD which

should result in a higher V_{OC} . As the V_{oc} depends on (i) the splitting of the Fermi levels for photogenerated charges, (ii) the recombination, and (iii) the energetics of the devices [14, 17, 18], the slightly lower voltage in devices fabricated with S101 as HTM might be due to high recombination which suggests S101 has slightly inferior charge extraction capability as compared to spiro-OMeTAD.

Figure 6.10 Current density vs. voltage curve under AM 1.5G illuminations (100 mWcm^{-2}).

Table 6.4 Summary of device parameters; open circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and efficiency (η). Area = 0.2 cm². Champion cell data is given in parentheses. Average data with standard deviation were based on ten cells.

HTM	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE
S101	18.66±0.41 (18.9)	0.915±0.005 (0.92)	63.2±1.69 (65)	10.75±0.25 (11)
Spiro-OMeTAD	19.68±0.27 (19.7)	0.966±0.007 (0.975)	63.05±1.02 (64.2)	12.0±0.28 (12.3)
W/O HTM	8.54	0.76	72	4.7

6.3.5 Steady state and time resolved PL quenching

To further elucidate the low V_{oc} obtained from S101 devices, the charge-carrier dynamics at the perovskite/ HTM interface and hole extraction ability were investigated using steady-state and time-resolved photoluminescence (PL) measurements, in which the efficient quenching of the steady-state PL and the reduction of the PL lifetime are indicators of efficient charge extraction at the perovskite/HTM interface. From the PL spectra (Fig. 6.11a), it is evident that both HTMs significantly quench perovskite emission signal, with HTM spiro-OMeTAD having a slightly better PL quenching efficiency ~ 93% as compared to S101, which has ~89%. Time-resolved PL measurements were carried out (at SPMS, NTU, by Dr. Annalisa Bruno) with excitation at 404 nm and monitoring of the entire emission spectral range (Fig. 6.11b). The pristine perovskite (CH₃NH₃PbI₃) exhibited a radiative life time of about 2.7 ns, whereas this was shorter in CH₃NH₃PbI₃/HTM samples. CH₃NH₃PbI₃/spiro-OMeTAD samples showed a decay time of 0.8 ns whereas CH₃NH₃PbI₃/S101 samples showed a longer decay life time of 1.1 ns. This indicates that spiro-OMeTAD has slightly better hole extraction ability as compared to S101. As a result it is unlikely that

further device optimization will enable the device performance of S101 to exceed that from spiro-OMeTAD-based devices. The values of 11% and 12.3% obtained from devices are below the current state-of-the-art values of over 20% but those values result from extensive optimization of the perovskite preparation and device fabrication. It is possible that with similar optimization efficiency values close to 20% might be attainable using S101. In that case, the much lower cost of S101, due to its simpler synthesis and comparable device performance might offer a potentially lower cost/power ratio which is the ultimate economic criterion for photovoltaic systems.

Figure 6.11 The steady-state photoluminescence (PL) spectra and (b) time-resolved PL spectra of CH₃NH₃PbI₃, CH₃NH₃PbI₃/S101 and CH₃NH₃PbI₃/spiro-OMeTAD.

Table 6.5 Time resolved photoluminescence characterization of the CH₃NH₃PbI₃ perovskite.

Sample	Fraction	τ_1 (ns)	Fraction	τ_2 (ns)	τ_{av} (ns)
CH ₃ NH ₃ PbI ₃	0.65	3.5	0.35	1.2	2.7
CH ₃ NH ₃ PbI ₃ /Spiro	0.64	0.78	0.36	0.71	0.8
CH ₃ NH ₃ PbI ₃ /S101	0.62	1.02	0.38	1.1	1.1

6.4 Conclusions and Outcome

A novel HTM S101 based on a silafluorene core has been synthesized by a short, low cost route and employed in perovskite as hole transporting layer. This is the first report of silafluorene based HTM for PSCs. The devices fabricated with HTM S101 shows a PCE of $\sim 11\%$ which is comparable to that ($\eta = 12.3\%$) obtained with the state of the HTM spiro-OMeTAD. It is probable that with further optimization and fine tuning of various device parameters and by developing more understanding of interfacial characteristics, there can be further significant enhancement in the device performance. The charge carrier dynamics study shows that S101 has significant hole quenching and extraction ability. In contrast to bulky spiro-OMeTAD, linear planar silafluorene-based HTM S101 has lower T_g but the performance comparable to spiro-OMeTAD. This suggests high T_g is not necessary for high efficiency, though more detailed device stability tests need to be performed to see if it is important for extending lifetime. The short, efficient synthesis and good device performance means S101 has potential to replace the more expensive spiro-OMeTAD. This work also lays out a strategy for the design and development of new cost effective and efficient HTMs for PSCs.

References

- [1] J. Hou, H. Y. Chen, S. Zhang, G. Li, and Y. Yang. *J. Am. Chem. Soc.* **2008**, 130, 16144-16145.
- [2] E. G. Wang, L. Wang, L. F. Lan, C. Luo, W. L. Zhuang, J. B. Peng, and Cao, *Appl. Phys. Lett.* **2008**, 92, 033307.
- [3] N. Blouin, A. Michaud, and M. Leclerc, *Adv. Mater.* **2007**, 19, 2295-2300.
- [4] M. Svensson, F. L. Zhang, S. C. Veenstra, W. J. H. Verhees, J. C. Hummelen, J. M. Kroon, O. Inganäs, and M. R. Andersson, *Adv. Mater.* **2003**, 15, 988-991.

- [5] D. Muhlbacher, M. Scharber, M. Morana, Z. G. Zhu, D. Waller, R. Gaudiana, and C. Brabec, *Adv. Mater.* **2006**, 18, 2884-2889.
- [6] W. Yue, Y. Zhao, S. Shao, H. K. Tian, Z. Y. Xie, Y. H. Geng, and F. S. J. Wang, *J. Mater. Chem.* 2009, 19, 2199-2206.
- [7] C. Duan, W. Cai, F. Huang, J. Zhang, M. Wang, T. Yang, C. Zhong, X. Gong, and Y. Cao, *Macromolecules* **2010**, 43, 5262-5268
- [8] M. C. Scharber, D. Wuhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, and C. J. Brabec. *Adv. Mater.* **2006**, 18, 789-794.
- [9] S. Yamaguchi, and K. Tamao, *J. Chem. Soc., Dalton Trans.* **1998**, 3693-3702.
- [10] G. Lu, H. Usta, C. Risko, L. Wang, A. Facchetti, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.* **2008**, 130, 7670-7685.
- [11] Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan, and A. J. Heeger, *Nat. Mater.* **2012**, 11, 44-48.
- [12] S. F. Chen, Y. Tian, J. Peng, H. Zhang, X. J. Feng, X. Xu, L. Li, and J. Guo, *J. Mater. Chem. C* **2015**, 3, 6822-6830.
- [13] A. El-Zohry, A. Orthaber and B. Zietz, *J. Phys. Chem. C* **2012**, 116, 26144-26153.
- [14] A. Krishna, D. Sabba, J. Yin, A. Bruno, P. P. Boix, Y. Gao, H. A. Dewi, G. G. Gurzadyan, C. Soci, S. G. Mhaisalkar, and A. C. Grimsdale, *Chem. Eur. J.* **2015**, 21, 15113-15117.
- [15] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.* **2011**, 23, 2367-2371.
- [16] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Science* **2012**, 338, 643-647.
- [17] N. J. Jeon, J. Lee, J. H. Noh, M. K. Nazeeruddin, M. Grätzel, and S. I. Seok, *J. Am. Chem. Soc.* **2013**, 135, 19087-19090.
- [18] A. Krishna, D. Sabba, H. Li, J. Yin, P. P. Boix, C. Soci, S. G. Mhaisalkar, and A. C. Grimsdale, *Chem. Sci.* **2014**, 5, 2702-2709.

Chapter 7

Discussion and Future Work

A summary of the work done is presented, and discussed in the context of the proposed hypotheses. The conclusions that can be drawn and the scientific insights gained are summarized. Suggestions for future work are presented to build upon the insights gained. Some preliminary work on possible future directions is also presented, which includes the design of several new HTMs based on stilbene, triptycene, adamantane, furan, silolothiophene and silafluorene cores. Some initial studies done on HTM (SB101) based on Stilbene core are also presented to demonstrate its qualification as an HTM. Finally further suggestions about future work are included.

7.1 Discussion and Summary

During the past two decades the solid-state mesoscopic solar cells (sMSCs) have emerged as the promising alternative to the conventional photovoltaic technologies. Recently organic–inorganic metal halide perovskites, in particular methyammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have emerged as very promising light harvesting materials for high performance and low cost photovoltaic technology. However, the high cost of spiro-OMeTAD and the often significantly lower performance of other HTMs are impeding the growth and advancement of high efficiency cost effective perovskite solar cells. Hence it is imperative to find alternative HTMs to spiro-OMeTAD, which have better or comparable efficiency and are more economical to produce. In this doctoral thesis, various HTMs based on different design principles have been studied and some potential principles for design of HTMs for achieving high photovoltaic performance have been established. To understand the fundamentals and working of the HTMs the charge carrier dynamics were studied which gave insights in to the working of HTMs.

- In Chapter 4 the synthesis of a series of novel hole transporting materials (T101, T102 and T103) based on a triptycene core with diarylamine, triarylamine and thiophene-linked triarylamine sidechains, respectively, is described. The bulky and twisted structure of triptycene has some similarity to that of spiro-OMeTAD and provides high thermal stability, high glass transition temperature (T_g) and high solubility in common organic solvents. The opto-electronic properties of the HTMs were theoretically estimated from the quantum calculations and were found to be consistent with the experimental data. T102 and T103 exhibited extended π -conjugation due to insertion of phenyl ring between the triptycene and diphenylamine moieties in T102 and the thienyl group in T103. Their absorption spectra showed red shift due to the extended π -conjugation. The T_g of the all the three HTMs

are over 100°C, which is attributed to the rigid and bulky nature of the triptycene core. The PCE of the device with T101, T102, and T103 as HTM was 8.42%, 12.24% and 12.38%, respectively. In comparison the device incorporating spiro-OMeTAD as HTM showed PCE of 12.87%. This means that T102 and T103 are similar in performance to spiro-OMeTAD but are much cheaper to make. These results show that performance of these three materials in perovskite solar cells was profoundly influenced by the sidechains. To elucidate the difference in performance of these HTMs electrochemical impedance spectroscopy was performed. It was observed that devices with T102 have high recombination resistance and low series resistance which attributed for its high V_{OC} and FF. However, T102 has lower J_{SC} than T103, which can be attributed to the poor injection to perovskite/T102 due to its deeper HOMO level. The discovery of triptycene-based high performance HTMs for PSCs opens new avenues in the design and synthesis of HTMs for PSCs. This work clearly demonstrates and highlights the role of the side chains on the performance of the PSC device. Hence the nature of both the core and side chains must be taken into consideration while designing a new HTM for high efficiency PSCs.

- In Chapter 5 is discussed the synthesis of a new furan based HTM (F101) consisting of an electron-rich furan core linked to triphenylamine moieties. The smaller size of the O atom in the ring compared to S in previously reported thiophene-based HTMs was expected to result in closer intermolecular π - π stacking, which could be beneficial for enhancing the hole transport and also increase the lifetime of charge carriers. The modelling data suggest F101 has good packing and mobility. Furthermore, the small molecular size of the HTM might lead to better pore filling of the mesoporous TiO_2 layer loaded perovskite. The theoretically estimated optoelectronic properties of the HTM estimated employing quantum calculations were found to be consistent with experimentally obtained

values. The electrochemical characterization showed that it has a HOMO level similar to spiro-OMeTAD. The devices based on F101 produced high power conversion efficiency (PCE) of 13.2%, which was higher than the efficiency, obtained using spiro-OMeTAD (13%) as HTM. The F101 HTM based device exhibited a J_{SC} of 19.63 mA/cm² and a remarkably high V_{OC} of 1.1 V. The standard spiro-OMeTAD based device showed a J_{SC} ~ 18.4 mA/cm² and V_{OC} of 1.05 V, which were inferior to the F101 based device. The charge carrier dynamics of perovskite/HTM interface which gives insight into the charge transfer process were studied via steady state and time resolved PL. From PL steady state spectra, it was evident that both HTMs significantly quench perovskite emission signal, with HTM F101 demonstrating slightly better PL quenching efficiency, ~ 97%, compared to spiro-OMeTAD one ~ 93%. Both HTMs spiro-OMeTAD and F101 showed similar decay lifetime of ~ 1 ns. This proves that charge pairs generated upon illumination in perovskite are efficiently separated at the perovskite/HTM and then transferred to the HTM. The first furan based HTM (F101) has been made and tested, and while further studies need to be done on the pore filling and the interface, these results suggest that furan is potentially an excellent unit for incorporation in HTMs and furans should be further investigated as replacements for thiophene units in HTMs.

- In Chapter 6 is discussed synthesis of a novel HTM (S101) based on an electron rich silafluorene core to which are linked triphenylamine moieties, with hexyl chains attached to the silicon atom to produce high solubility inorganic solvents and so improve processing. The S101 molecule has a planar structure which is desirable for promoting intramolecular π -delocalization and intermolecular π - π stacking, which favour both charge carrier mobility and lifetime, boosting device efficiency. Quantum calculations were done to predict the opto-electronic properties of the HTM and were consistent with the experimental data. Differential scanning

calorimetry (DSC) showed S101 has a weak glass transition (T_g) at 45 °C which is quite low compared to spiro-OMeTAD ($T_g = 124$ °C). The electrochemical characterization showed that it has a deeper HOMO level compared to spiro-OMeTAD, but this did not produce a lower V_{OC} . The devices fabricated with HTM S101 shows a PCE of $\sim 11\%$ which is comparable to that ($\eta = 12.3\%$) obtained with spiro-OMeTAD. The charge carrier dynamics of perovskite/ HTM interface which gives insight into the charge transfer processes were studied via steady state and time resolved PL. From the PL spectra it was evident that both HTMs significantly quench perovskite emission signal, with HTM spiro-OMeTAD having a slightly better PL quenching efficiency (93%) relative to S101 (89%). Time-resolved PL measurements of $CH_3NH_3PbI_3$ /spiro-OMeTAD samples showed a decay time of 0.8 ns whereas $CH_3NH_3PbI_3$ /S101 samples showed a longer decay life time of 1.1 ns. This indicates that both HTMs are quenching the holes but spiro-OMeTAD has a slightly better hole extraction ability as compared to S101. While device lifetimes have not been measured, these results suggest silafluorene derivatives can produce at least comparable to cost-per-unit power performance to spiro-OMeTAD. Hence, further molecular engineering can be done to make new derivatives of the HTM. Based on the work in this thesis, a couple of such derivative could be silafluorene linked to thienyltriphenylamine or furyltriphenylamine, as in the triptycene HTM study it was shown that thienyltriphenylamine has been proven to perform better TPA alone and in chapter 5 it was shown that furans are promising replacements for thiophenes.

In summary the research led to several outcomes in terms of design principles which are listed below:

- The first class of HTMs (T101, T102 and T103) based on a triptycene core have been synthesized and tested as HTMs in mesoscopic perovskite solar cells. The results obtained from these HTMs show that the choice of functional sidegroup and/or linker has major effects on device performance thus helping to establish design principles for high performance HTMs. Thienyltriphenylamine groups gave the best results. It is also reported that there can be an interaction between the thiophene and the perovskite surface, possibly mediated by the thiophene iodine interaction, which may suggest a stronger adhesion and enhanced interfacial coupling between HTM and perovskite [1]. This may lead to effective hole transfer, hence thienyltriphenylamine can be used instead of just TPA moieties.
- The methoxy groups in TPA moieties play a critical role in the performance of the HTM. They improve the solubility of the HTM which is extremely important as the PSCs are solution processed. Also methoxy groups raise the HOMO level which helps in band alignment between perovskite/HTM and promotes high driving force for hole transfer from perovskite.
- The first furan based HTM (F101) has been made and tested. The results suggest that furans should be further investigated as replacements for thiophene units in HTMs.
- The first silafluorene-based HTM (S101) has been made which has a deep HOMO energy level but shows slightly inferior device results to spiro-OMeTAD, suggesting that further structural modification is needed to produce a material with high performance.
- Comparison of results obtained from the new materials suggests that T_g may not be a critical factor for the design of new HTMs. Modulation of the HOMO levels by incorporation of thiophene or furan units seems to be a more promising approach. It has also been found that simulation can

provide useful insights into charge carrier mobility and device performance trends thus enabling pre-screening of plausible structures.

In conclusion, HTMs based on different design principles were synthesized and their properties and device performances studied in detail. The triptycene based HTMs are bulky, star shaped and non-planar with high T_g . By contrast the furan and silafluorene-based HTMs, i.e., F101 and S101 are linear and planar, respectively and possess lower T_g . This suggests high T_g is not necessary for high efficiency, though more detailed device stability tests need to be performed to see if it is important for extending lifetime. The performance of all these molecules having different dimensional symmetry (star shaped, linear and planar molecules) in PSCs is quite encouraging for the development of cost effective technologies. From the current study it clearly emerges that the key parameters which should be taken into consideration while designing an HTM are (i) proper HOMO level for hole injection, (ii) moderate hole mobility, (iii) high solubility in organic solvents, and (iv) optical and thermal stability.

7.2 Preliminary work and suggestions for future work

HTMs with different kind of cores have been synthesized. Here it is shown that different kinds of molecules can be used as efficient HTMs in PSCs. Initially when this PhD work was started the focus was on spiro-like molecules with high T_g . Triptycene based HTMs were bulky and had high T_g . Later good results appeared using linear planar molecules which have better π - π stacking which can enhance charge transport. HTMs F101 and S101 are linear and planar molecules. In future work also it is suggested that planar molecules which have simple structure and are easy to synthesize be prioritized.

7.2.1 Stilbene based linear HTM (SB101)

An electron rich stilbene core has been linked to TPA moieties to give HTM SB101 (Fig. 7.1). Stilbene core was selected as it is relatively inexpensive when compared to Spiro-OMeTAD. Furthermore, stilbene has a linear planer structure which suggests that closer intermolecular π - π stacking is possible for this stilbene core HTM. The idea behind structure of SB101 is similar to F101. This will facilitate intermolecular charge transport. Stilbene also shows high solubility in organic solvents. The high solubility is essential in the fabrication of perovskite solar cells as the HTM is normally deposited on the device surface through spin coating process and having high organic solubility will allow higher quality film to be produced, which can boost the efficiency of perovskite solar cell.

Figure 7.1 Chemical structure of SB101.

The synthesis route of SB101 is very much shorter and less expensive as compared to spiro-OMeTAD (Fig. 7.2). The commercially available relatively inexpensive stilbene was Suzuki coupled with triphenylamine boronic acid derivative to give SB101 with high yield as shown in Fig. 7.2.

Figure 7.2 Synthetic route of SB101.

Trans-4, 4'-dibromostilbene (250 mg, 0.74 mmol), {4-[bis(4-methoxyphenyl)amino]phenyl}boronic acid (560 mg, 1.6 mmol), [Pd(PPh₃)₄] (80 mg, 0.07 mmol), K₂CO₃ (5 mL, 2M) and degassed toluene (20 mL) were transferred in to a 50 mL round-bottomed flask. The reaction mixture was then stirred and heated at 90 °C for 72 hours. The reaction mixture obtained was then cooled before extracting with dichloromethane (DCM). The extract was then passed through anhydrous MgSO₄ to remove any water. The mixture was then concentrated and was purified with column chromatography on silica with DCM:hexane ratio of 3:2(v:v). The collected product was dried in a vacuum oven for 24 hours at a room temperature to obtain the resultant SB101 as a neon yellow powdered solid (310mg, 54% yield).

¹H NMR (CDCl₃, 400 MHz): δ =7.558 (d, 8H), 7.458 (d, J=8.8 Hz, 4H), 7.147 (s, 2H), 7.108 (d, J=8.8 Hz, 8H), 7.006 (d, J=8.8 Hz, 4H), 6.826 (d, J=8.8 Hz, 8H), 3.809 (s, 12H). HRMS (MALDI-TOF): m/z calcd for C₅₄H₄₆N₂O₄, 786.9; found: 785.9.

Figure 7.3 ¹H NMR spectra of SB101.

Figure 7.4 MALDI-TOF mass spectra of SB101.

Figure 7.5 Quantum Modeling for SB101 showing distribution of HOMO and LUMO state.

Fig.7.5 shows the chemical structure of the SB101 and the electronic density distribution of the frontier orbitals calculated by density functional theory (DFT). For SB101, the highest occupied molecular orbital (HOMO) level shows π -bonding character, spreading over the whole molecule; while lowest unoccupied molecular orbital (LUMO) shows π^* -antibonding character being predominately localized on the central stilbene core and two benzene units. The calculated hole reorganization energy for SB101 is 0.129 eV which is lower than of spiro-OMeTAD (0.148 eV), which suggest that SB101 is a good potential HTM for perovskite solar cells.

Figure 7.6 (a) Absorption Spectra for Spiro-OMeTAD and S101; (b): Cyclic voltammogram for Spiro-OMeTAD and SB101.

The UV-visible absorption spectra of SB101 and spiro-OMeTAD are shown in Fig. 7.6a. The onset absorption wavelength of SB101 and Spiro-OMeTAD were 454nm and 420nm respectively. The onset of absorption of SB101 is red shifted as compared to spiro-OMeTAD which suggests that SB101 has better π -conjugation. Cyclic voltammogram of SB101 with reference to ferrocene is shown in Fig. 7.6b. SB101 exhibits reversible redox peaks showing good electrochemical stability. The HOMO energy level calculated from CV is -5.37eV whereas the HOMO of spiro-OMeTAD is -5.22eV. The reported HOMO energy level for $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite is -5.44 eV, which indicates that HTM SB101 have energetics favorable for hole transfer. As the difference in energy level from the Fermi level of TiO_2 and the HOMO of the HTM determines the open circuit voltage (V_{OC}) of the device, a deeper HOMO value will then correlate to a higher V_{OC} , so higher V_{OC} can be expected in SB101 HTM based devices. Table 1 summarizes the optical and electrochemical properties of SB101.

Table 7.1 Optical and electrochemical properties of SB101.

HTM	LUMO (eV)	HOMO (eV)	λ_{hole} (eV)	E_g (eV)	λ_{max} (nm)	λ_{onset} (nm)
SB101	-2.67	-5.37	0.129	2.75	392	454
Spiro-OMeTAD	-2.27	-5.22	0.148	2.95	383	420

The preliminary optical and electrochemical investigations of SB101 demonstrate that this material has excellent properties which qualify it for application as HTM in PSCs. This material has been sent to the laboratory of Professor Henk Bolink in University of Valencia, Spain for fabrication and testing of devices.

7.2.2 Triptycene Based HTM (T104)

It was shown in chapter 4 that triptycene based HTMs perform exceedingly well in PSCs. Here I propose an HTM T104 (Fig.7.7) which is similar to T103, but instead of thiophene it has a furan ring between the triptycene and TPA moieties. In chapter 5 I showed that furan can be used as the core of a high performance HTM and suggested furans could be possible replacements for thiophenes in other HTMs. Hence it would be logical to investigate the effect of incorporating a furan into the previously developed triptycene based HTM.

Figure 7.7 Chemical structure of T104.

7.2.3 Adamantane Based HTM

Two novel HTMs A101 and A102 (shown in Fig. 7.8) based on adamantane core is proposed. Adamantane is bulky in nature and HTMs based on adamantane are expected to show amorphous nature, good thermal stability, high T_g and good film forming ability. From our earlier studies on triptycene based HTMs in chapter 4, it was demonstrated that thienyltriphenylamine sidegroup perform better than TPA groups alone, so the adamantane core is linked to TPA moieties via thiophene or furan ring. Also it's been recently reported that the number of TPA side groups affect the performance. Park et al. [2] reported that tetra-TPA

substituted HTMs with papracyclophane cores performed better than the corresponding di-TPA and tri-TPA substituted cyclophanes. The proposed adamantane HTMs A101 and A102 are tetrasubstituted.

Figure 7.8 Chemical structures of HTMs A101 and A102.

7.2.3 Furan Based HTMs

As discussed in chapter 5, furan based HTM F101 showed exceptionally good performance outperforming spiro-OMeTAD while being much simpler in design and synthesis. Here a HTM F102 (Fig. 7.9) which is a derivative of furan based HTM F101 is proposed. In this HTM F102 all the four positions in the furan ring are substituted by the TPA side group. F102 will be more bulky than the F101, so we can expect a high T_g and also it has more number of TPA side groups, so the effect of these extra TPA on the property and performance can be studied. The corresponding tetrasubstituted thiophene has been previously found to give even better performance than spiro-OMeTAD [3] and it would be logical to see how the furan derivative compares with it.

Figure 7.9 Chemical structure of HTM F102.

7.2.4 Organo-silicon based HTMs

As discussed in chapter 6, silafluorene based HTM S101 showed slightly lower performance than spiro-OMeTAD but is much simpler in design and synthesis. To improve the properties and performance of HTM S101 design strategies are applied and new derivatives (S102, S103, S104 and S105) of S101 are proposed as shown in Fig. 7.10. In HTMs S102 and S103 thiophene and furan groups are inserted between the silafluorene core and the TPA functional group. In S104 and S105, silolothiophene core is introduced. Thienyltriphenylamine and furyltriphenylamine are linked to this silolothiophene core to give HTM S104 and S105, respectively.

Figure 7.10 Chemical structures of HTM S102-S105.

The further studies focused on the synthesis, structural, thermal, electrochemical and optical characterization of the above proposed materials along with the quantum calculations to theoretically estimate their physical properties must be carried out prior to their use in PSCs. The incorporation of these possible new HTMs designed on the basis of the insights developed and the design principle evolved during the course of the current work is expected to yield several new aspects of the HTMs in general and the charge carrier dynamics of the perovskite/HTM interface in particular.

References

- [1] M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J.-P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K.-H. Dahmen, F. De Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel, and M. K. Nazeeruddin, *Nat. Energy* **2016**, 1, 15017.
- [2] S Park, J. H. Heo, J. H. Yun, T. S. Jung, K. Kwak, M. J. Ko, C. H. Cheon, J. Y. Kim, S. H. Im, and H. J. Son, *Chem. Sci.* **2016**, 7, 5517-5522.
- [3] H. Li , K. Fu , P. P. Boix , L. H. Wong , A. Hagfeldt , M. Grätzel, S. G. Mhaisalkar , and A. C. Grimsdale, *ChemSusChem* **2014**, 7, 3420-3425.

APPENDIX

List of Publications

1. A. Krishna, D. Sabba, Jun Yin, A. Bruno, L. J. Antila, C. Soci, S. Mhaisalkar, A. C. Grimsdale, "Facile Synthesis of Hole Transporting Material with Silafluorene Core for Efficient Mesoscopic CH₃NH₃PbI₃ Perovskite Solar Cells"- *J. Mater. Chem. A* **2016**, 4, 8750-8754.
2. A. Krishna, D. Sabba, Y. Jun, A. Bruno, P. P. Boix, H. A. Devi, G. Yang, G. Gurzadyan, C. Soci, S. Mhaisalkar, A. C. Grimsdale, "Facile Synthesis of a Furan-Arylamine Hole Transporting Material for High Efficiency Mesoscopic Perovskite Solar Cells"- *Chem. Eur. J***2015**, 21, 15113-15117.
3. T. Salim, S. Sun, Y. Abe, A. Krishna, A. C Grimsdale, Y. M. Lam, "Perovskite-Based Solar Cells: Impact of Morphology and Device Architecture on Device Performance" – *J. Mater. Chem. A***2015**, 3, 8943-8969.
4. J. Yin, D. Cortecchia, A. Krishna, S. Chen, N. Mathews, A. C Grimsdale, C. Soci, "Interfacial Charge Transfer Anisotropy in Polycrystalline Lead Iodide Perovskite Films" – *J. Phys. Chem. Lett.* **2015**, 6 (8), 1396-1402.
5. A. Krishna, D. Sabba, H. Li, J. Yin, P. P. Boix, C. Soci, S. G Mhaisalkar, A. C Grimsdale, "Novel hole transporting materials based on triptycene core for high efficiency mesoscopic perovskite solar cells" - *Chem. Sci.***2014**, 5, 2702-2709. Featured as Hot article in Chemical Science Blog, RSC and most downloaded article for April – June 2014 quarter.

6. A. Krishna, A. V. Lunchev and A. C. Grimsdale, “Suzuki Polycondensation”, in *Modern Synthetic Methods for Conjugated Polymers and Carbon Materials*, (Eds. M. Leclerc, J-F. Morin, Wiley-VCH, ISBN: 978-3-527-33998-3, press date Jan 2017) [Invited Book Chapter].

Cost Analysis of Triptycene based HTMs

The detailed comparisons between the synthesis of triptycene based HTM and spiro-OMeTAD are discussed here, in terms of number of steps, yields of each step, cost of starting materials and total reaction time. As shown in the **Scheme A1**, the comparisons are actually focusing on the synthesis of tetrabromo-spirofluorene core (compound **6**) and triiodotriptycene core (compound **13**). The data were summarized in **Table A1**.

First of all, in both cases four steps are needed to achieve targeting molecules from readily available and cheap starting materials, in another word, we can purchase instead of synthesizing these starting materials for scaling-up purpose. Moreover, the equal number of steps makes the comparison easier. The prices were quoted from Alfa Aesar US website with the largest possible package size available for fair comparison. All the prices are in USD. The costs of solvents and reagents used in both routes such as THF, DMF, acids, salts, etc. were assumed to be cancelled out each other because they are very common chemicals in a typical chemistry lab and both have equal number of steps. Coincidentally, the MWs of both core **6** and **13** are 632, therefore we can easily compare both based on mass which can be equivalently translated to mole.

In order to make 10 g of core **6**, the amount of compound **1** and **3** consumed, calculated from the yield of each step, is 9.0 g and 9.1 g, respectively. The unit price of compound **1** and **3**, is \$95.4/5g and \$556/2.5kg, respectively. As a result, the total cost of starting materials for making core **6** is \$173.7/10g. For your

information, the price of spiro-OMeTAD from Merck, one of the few licensed companies, is about SGD 1066/g, equal to \$850/g. In the same way, the total cost of starting materials for making core **13** is \$12.5/10g (compound **7**: \$225/5kg; compound **8**: \$557/5kg; compound **9**: \$115/500mL; Pd/C: \$125/100g). It is very clear to see the material costs of making core **13** is almost 14 times less than that of core **6**. The difference will be rather considerable when scaling up.

The total duration time of the reactions from first step to the end is an important factor to estimate the timeline for production. As we can see from **Table S1** that the total reaction time for making core **13** is almost half of the amount of time for making core **6**. Especially synthesizing compound **12** and core **13** only take 2 hours each from their respective precursors; it is possible to finish both steps within one day. Since both have four steps, it can easily conclude that it is faster to make core **13** than core **6**, which not only saves the time but also saves the manpower which is much more expensive.

In short, we can confirm that making core **13** is cheaper than core **6**.

Table A1. Summary of the cost analysis of spiro and triptycene core.

	total cost of starting materials	number of steps	total duration time of reactions	estimated number of days to complete the whole process
Core 6	\$173.7/10g	4	61.5 hours	5 days
Core 13	\$12.5/10g	4	32.25 hours	3 days

Scheme A1. Synthetic schemes to the core **6** and **13**, with reaction condition, duration of time and yield of each step indicated.

Cost Analysis of Silafluorene based HTMs

The detailed comparisons between the synthesis of Silole based HTM and spiro-OMeTAD are discussed here, in terms of number of steps, yields of each step, cost of starting materials and total reaction time. As shown in the Scheme A2, the comparisons are actually focusing on the synthesis of tetrabromo-spirofluorene core (compound **6**) and S101 core 3,7-(dibromo-5,5-dihexyl-5H-dibenzo[b,d]silole) (compound **12**). The data is summarized in Table A2.

Scheme A2. Synthetic schemes to the core **6** and **12**, with reaction condition, duration of time and yield of each step indicated.

First of all, in both cases four steps are needed to achieve core molecules from readily available and cheap starting materials. Moreover, the equal number of steps makes the comparison easier. The prices were quoted from Alfa Aesar US website and Fluorochem UK with the largest possible package size available for fair comparison. All the prices are in USD. The costs of solvents and reagents used in both routes such as THF, DMF, acids, salts, etc. were assumed to be approximately the same - these are very common and inexpensive chemicals and there is an equal number of steps.

In order to make 10 g of (spiro) core **6**, the amount of compound **1** and **3** consumed, calculated from the yield of each step, is 9.0 g and 9.1 g, respectively. The unit price of compound **1** and **3**, is \$76.3/5g and \$580/2.5kg, respectively. As a result, the total cost of starting materials for making core **6** is \$139.5/10g. For comparison, the price of spiro-OMeTAD from Merck, one of the few licensed companies, is about \$850/g. In the same way, in order to make 10 g of (S101) core **12**, the amount of compound **7** and **11** consumed, calculated from the yield of each step, is 20.7 g and 9.3 g, respectively. The unit price of compound **7** and **11**, is \$135.9/100g and \$271/50g, respectively. As a result, the total cost of starting materials for making core **12** ~ \$76/10g. The difference will be rather considerable when scaled up.

The total duration time of the reactions from first step to the end is an important factor to estimate the timeline for production. As we can see from **Table S1** that the total reaction time for making core **12** is almost half of the amount of time for making core **6**. Since both have four steps, it can easily conclude that it is faster to make core **12** than core **6**, which not only saves the time but also saves the manpower which is much more expensive.

In short, we can confirm that making core **12** is cheaper than core **6**. In addition the purification of spiro-OMeTAD requires expensive sublimation, whereas S101 can be purified by cheaper methods such as column chromatography.

Table A2. Summary of the cost analysis of spiro and silafluorene core.

	total cost of starting materials	number of steps	total duration time of reactions	estimated number of days to complete the whole process
Core 6	\$139.5/10g	4	59.5 hours	5 days
Core 12	\$76/10g	4	27 hours	3 days